PB90-246091

Evaluation of an Anion Exchange Resin for Sampling Ambient Level Phenolic Compounds

Battelle Columbus Div., OH

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

27 Apr 90

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before comple

1. REPORT NO. EPA/600/3-90/055

2.

3 PB90-246091

4. TITLE AND SUBTITLE
Evaluation of an Anion Exchange Resin for Sampling Ambient Level Phenolic Compounds

5. REPORT DATE April 27, 1990

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Marcia Nishioka and Hazel Burkholder

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Battelle
505 King Avenue
Columbus, Ohio 43201

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO. 68-02-4127

12. SPONSORING AGENCY NAME AND ADDRESS
AREAL
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED EPA 12/1/88 - 9/30/89

14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The determination of human exposure to polar volatile and semivolatile organic compounds is an area of increasing importance to EPA. Since the bioavailability of many polar compounds is greater than for relatively non-polar compounds, methods are needed for the selective sampling and analysis of these types of compounds. The anion exchange resin AG MP-1 was evaluated for selective collection and retention of vapor phase phenolic compounds. The primary goal of the program was development of sampling and analysis conditions which would permit detection and quantification of diverse phenolic and hydroxylated species at ambient levels of 1 ppbv. Phenols (and other acidic compounds) are retained on AG MP-1 by formation of a chemical bond; the reaction is reversed to liberate the phenols from the sorbent prior to analysis. Because of the dominant concern about collection and recovery, investigations here centered upon those parameters which affect the formation of the initial chemical bond between phenolic analyte and sorbent and those procedures that allow subsequent reversal of these reactions for quantitative recovery of analytes in the laboratory.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Phenol Phenolic Compounds Anion Exchange Trace-level Ambient Level Sampling		

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21. NO. OF PAGES**
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB90-246091
EPA/600/3-90/055
April 1990

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Contract No. 68-02-4127/ WA 69 and 80

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April 27, 1990

ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an indepth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to polar semivolatile organic compounds is an area of increasing importance to EPA. Since the bioavailability of many polar compounds is greater than for relatively non-polar compounds, methods are needed for the selective sampling and analysis of these types of compounds. The sorbent sampler described in this report provides a new capability of sampling for acidic and phenolic vapor phase organic compounds.

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ABSTRACT

The currently available method for collection of vapor phase phenol and methyl-phenols involves aqueous sodium hydroxide impinger collection. Solution sampling is, in general, not practical for field sampling at remote sites; in addition, this impinger method has not been evaluated for collection of chemically diverse and more toxic phenolic species such as the chloro- and nitro-phenols. Sorbent based sampling methods are preferable to impinger methods.

The program described here was designed for evaluation of a solid sorbent, the anion exchange resin AG MP-1, for selective collection and retention of vapor phase phenolic compounds. The primary goal of the program was development of sampling and analysis conditions which would permit detection and quantification of diverse phenolic and hydroxylated species at ambient levels of 1 ppbv. Phenols (and other acidic compounds) are retained on AG MP-1 by formation of a chemical bond; the reaction is reversed to liberate the phenols from the sorbent prior to analysis. Because formation of the chemical bond ensures retention of analytes, retention is the lesser important of the two considerations. Because of the dominant concern about collection, investigations here centered upon those parameters which affected the formation of the initial chemical bond between phenolic analyte and sorbent.

On this program we measured an average recovery of 89% (82-101%) for 1 μg quantities of 13 chemically-diverse phenolic compounds that were spiked into a heated gas stream, sampled at 100 mL/min through AG MP-1, extracted from the AG MP-1, and concentrated prior to analysis. Recovery of a solution spike of these analytes to AG MP-1 without subsequent gas sampling averaged 85% (76-104%). Because recoveries from the two spiking experiments were comparable, we concluded that vapor phase collection was essentially quantitative. Sorbent mesh size and superficial linear sampling velocity were those parameters which affected collection efficiency most dramatically. Sampling was most efficient with the 200-400 mesh AG MP-1 (particle diameter range of 38-75 um) at a linear velocity of 1.75 cm/sec. Field-collected samples showed that neutral species such as aliphatic and aromatic hydrocarbons were retained by this

sorbent in addition to the phenolic and acidic species. For this reason, extraction methods were developed for selective extraction of neutral species prior to extraction of phenols. These methods were developed for neutral specie levels 1000 times greater than anticipated phenol levels and resulted in greater than 90% recovery of spiked neutral species.

Field sampling with the AG MP-1 sorbent was carried out at two locations in the northern Delaware area and at three locations in the Columbus, Ohio area. Analyses of field-collected samples were performed using gas chromatography/mass spectrometry with electron impact ionization (EI GC/MS) and methane negative chemical ionization (NCI GC/MS). Three native phenols were detected and quantified in the Delaware-collected samples at levels of 0.6-60 $\mu g/m^3$. The sorbent tube used as a passive sampler contained native phenol levels similar to the levels obtained with the sorbents sampled at 20 and 100 mL/min. These results indicated that this sorbent material may be used effectively in passive samplers of proper design. Lab blanks showed minimal levels of one analyte (phenol) detected in field samples. The field blank contained relatively high levels of phenol and one other phenolic analyte, 3- and/or 4-OH-benzaldehyde; except for phenol, calculated ambient levels for the native analytes were greater than the field blank levels, indicating that these analytes were, indeed, present at significant levels. Some channeling of the air stream through the sorbent may have occurred; although higher quantities of each analyte were collected at the 100 mL/min sampling rate (relative to the 20 mL/min sampling rate), the calculated ambient concentrations were significantly higher from data obtained with the sorbent at the 20 mL/min sampling rate. Since significant losses occurred during the concentration steps used for these samples, these differences may not be valid in comparison of collection efficiency of the sorbent.

The sample collected in the Battelle parking lot, reflecting primarily automotive emissions, was analyzed for tentative identification of those compound classes which may be collected in urban atmospheres by AG MP-1. Aliphatic carboxylic acids and alkyl-phenols were the dominant species detected using EI GC/MS. The NCI GC/MS analysis, which provided selective and sensitive detection of electronegative compounds, produced numerous spectra suggestive of hydroxylated nitro-aromatic ($OH\text{-}NO_2\text{-}$)

compounds. The spectrum of one compound suggests OH-diNO_2-substitution of the azaarene cinnoline. Tentative identification of this OH-diNO_2-cinnoline represents the first reporting of a OH-diNO_2-aromatic compound in an environmental sample.

On the basis of the results of this program we recommend that further laboratory studies be undertaken to verify collection of phenols from very dilute sample streams with collection over 12-24 hr sampling intervals. In addition, we recommend that AG MP-1 sorbent samplers be developed for passive sampling, and dynamic sampling at rates of 1, 10 and 100 L/min.

This report is being submitted in fulfillment of Contract No. 68-02-4127 (WA-69 and WA-80) by Battelle under the sponsorship of the US EPA. It covers a period of December 1, 1988 to September 30, 1989 and work was completed as of September 30, 1989.

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SECTION 1
INTRODUCTION

The currently available method for collection of vapor phase phenol and methyl-phenols involves aqueous sodium hydroxide impinger collection.[1] Solution sampling is, in general, not practical for field sampling at remote sites; in addition, this impinger method has not been evaluated for collection of chemically diverse and more toxic phenolic species such as the chloro- and nitro-phenols. Sorbent based sampling methods are preferable to impinger methods. As an alternative to the impinger method, PUF (polyurethane foam)-Tenax-PUF sandwich sorbent cartridges have been evaluated recently for the collection of vapor phase chloro-phenols.[2] While this method provides high collection efficiencies for the tetra- and pentachlorophenols, mono-chloro-phenols are not retained. These collection differences suggest that phenol and mono-functional phenols (e.g. methyl-phenols, nitro-phenols) also will not be retained by this sorbent.

The program described here was designed for evaluation of a solid sorbent, the anion exchange resin AG MP-1, for selective collection and retention of vapor phase phenolic compounds. The primary goal of the program was development of sampling and analysis conditions which would permit detection and quantification of diverse phenolic and hydroxylated species at ambient levels of 1 ppbv. The program also included 1) the development of methods for removing potential neutral interference compounds which could be retained by adsorption to the sorbent polymer backbone, 2) evaluation of stability of sorbent-bound analytes during prolonged storage, and 3) stability of sorbent-bound analytes toward nitration by ambient HNO_3. In addition, the program included preliminary field sampling evaluation of the sorbent. Field collection was carried out at two sites in northern Delaware; three additional samples were collected in the Columbus, Ohio area.

Anion exchange resins/sorbents are typically suspended in aqueous or organic media for chromatographic separations. For the strongly basic anion exchange resins, such as AG MP-1, the charge is fixed by the structure of the resin; positively charged quaternary amine groups are chemically bound to a styrene divinylbenzene lattice; the negatively charged counterion to the amine can be exchanged. The quaternary amine retains its charge whether or not the resin is suspended in solution. AG MP-1, available from Bio-Rad Laboratories, is a macroporous strong anion exchange resin. Because of the highly crosslinked and relatively rigid styrene divinylbenzene backbone, AG MP-1 does not shrink or swell excessively during extraction of analytes with solvents and is not crushed easily during sampling and handling. The high degree of porosity allows retention of larger, less polar organic acids and phenols so as to increase contact time for formation of the chemical bond between analyte and quaternary amine. AG MP-1 is similar to the XAD-2 resins in physical properties such as ease of handling, mechanical strength, and color. Further description of the resin is provided in Table 1.1

For sorbent sampling based upon adsorption, as with XAD-2, collection and retention are both described by chromatographic theory, the dominant factor being partition of analyte between gas and solid phase. For the anion exchange resin evaluated here, collection and retention are two separate issues. Phenols (and other acidic compounds) are retained on AG MP-1 by formation of a chemical bond; the reaction is reversed to liberate the phenols from the sorbent prior to analysis. Schematic representation of these steps is shown in Figure 1.1. For experiments conducted on this program, AG MP-1 was converted from the manufacturer-supplied Cl^- form to the OH^- form to obtain the strongest possible aqueous base (OH^-) for exchange. The OH^- on the resin will readily abstract a proton from phenolic and acidic organic analytes and thus effect attachment of an analyte anion to the quaternary amine exchange site. Analyte anions are displaced from the resin later by application of an acid of greater strength than the analytes, in this case 2% conc. HCl in 15:85 (v:v) methanol:methyl-t-butyl ether. Under these conditions the Cl^- form of the resin is generated and the organic analyte is regenerated as a neutral molecule. Because formation of the chemical bond ensures retention of analytes, retention is the lesser important of the two considerations. Phenols will be retained unless sampling occurs in atmospheres of very high HNO_3 concentrations (or other acid whose pKa is less than that of the phenols of interest) where HNO_3 may either displace phenols from the sorbent or nitrate the phenols and, thus, form artifacts. Because of the dominant concern about collection, investigations here have centered upon those parameters which affect the formation of the initial chemical bond between phenolic analyte and sorbent.

TABLE 1.1 DESCRIPTION OF AG MP-1

Manufacturer	BioRad Laboratories
Type	Strongly basic, anion exchanger
Lattice	Styrene divinylbenzene, 20% porosity
Active group	Quaternary amine, $R\text{-}CH_2\text{-}N^+(CH_3)_3$
Initial counter ion	Cl^-
Capacity	1.0 milliequivalent/mL
Density	0.7 gm/mL
Cost	$125/500 g

The target level for phenols in these laboratory experiments was 1 µg for each analyte. The 1 µg level represents the average quantity for phenols which, if present at 1 ppbv in the atmosphere, would be collected during a 24 hr period when sampling at 100 mL/min with 100% collection efficiency at ambient temperature and pressure. For phenols of interest, the quantity collected covers a range from 0.5 µg for phenol to 1.5 µg for pentachlorophenol. The target level for analysis in these laboratory experiments has been 1 ng/µL. This quantification level is required for the analysis of the 1 µg spike quantities when fully recovered and concentrated to a 1 mL volume.

After collection and prior to analysis, phenols are subjected to two extraction procedures: extraction from AG MP-1 with an acidified solvent and then extraction from that acidified sorbent eluate into a neutral solvent. As seen in the organization of both Methods and Results sections of this report, the experimental plan for the program involved, in sequence: (1) development and evaluation of GC and GC/MS analysis conditions; (2) evaluation of methods to extract phenols from acidified sorbent eluate; (3) evaluation of methods to extract phenols (and neutral compounds) from sorbent; (4) evaluation of parameters which affect collection of vapor phase phenols, and finally; (5) analysis of field-collected samples.

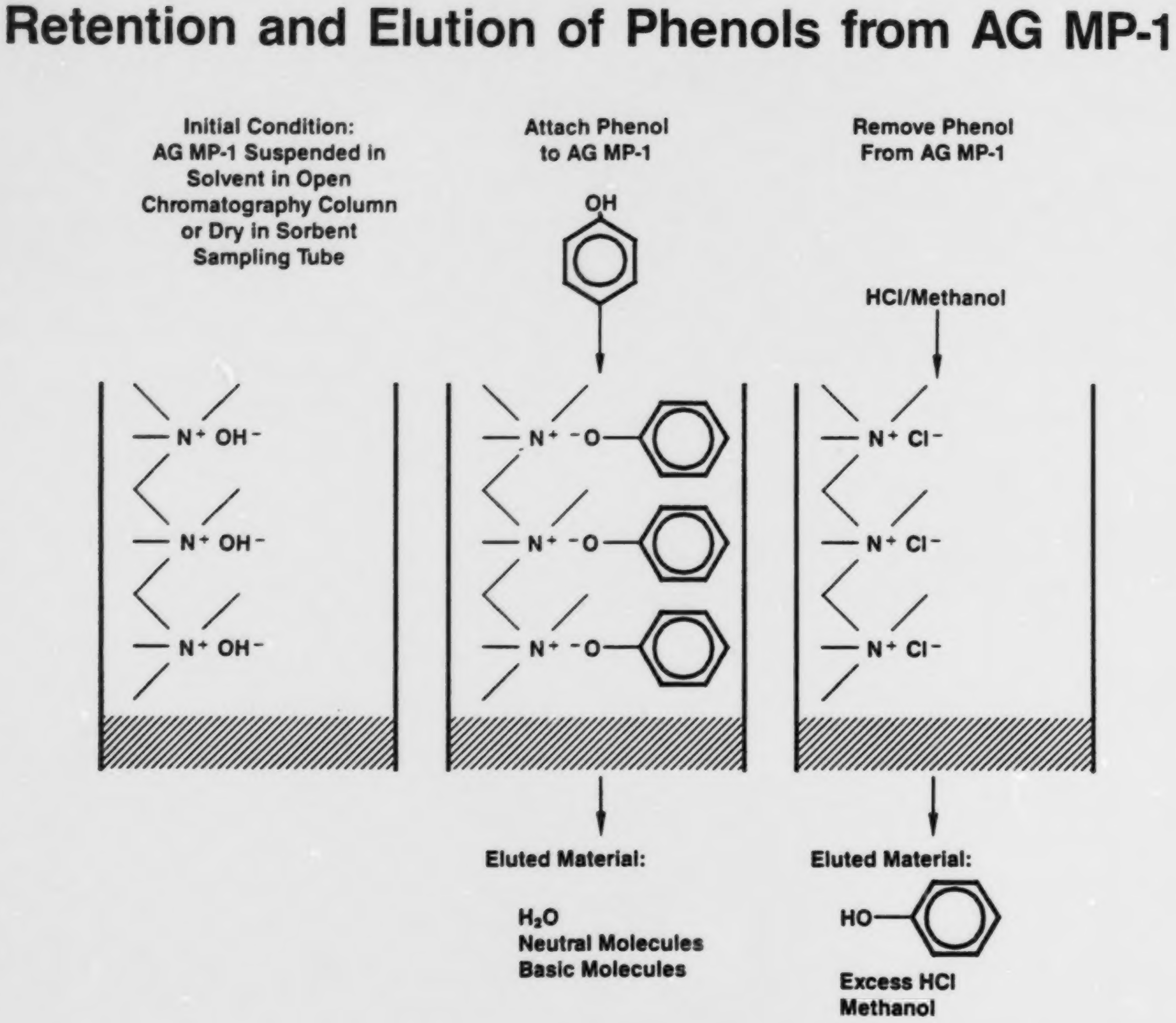

Retention and Elution of Phenols from AG MP-1
Initial Condition: AG MP-1 Suspended in Solvent in Open Chromatography Column or Dry in Sorbent Sampling Tube
Attach Phenol to AG MP-1
Remove Phenol From AG MP-1
OH
HCl/Methanol
N+ OH−
N+ −O
N+ Cl−
Eluted Material:
H₂O
Neutral Molecules
Basic Molecules
Eluted Material:
HO
Excess HCl
Methanol

Figure 1.1 Schematic Representation of Collection of Phenols with AG MP-1 and Subsequent Elution

SECTION 2
CONCLUSIONS

On this program we measured an average recovery of 89% (82-101%) for 1 µg quantities of 13 chemically-diverse phenolic compounds spiked into a heated gas stream and subsequently sampled at 100 mL/min through AG MP-1. Recovery of a solution spike of these analytes to AG MP-1 without subsequent gas sampling averaged 85% (76-104%). Because recoveries from the two spiking experiments were comparable, we concluded that vapor phase collection was essentially quantitative. Sorbent mesh size and linear sampling velocity were those parameters which affected collection efficiency most dramatically. Sampling was most efficient with the 200-400 mesh AG MP-1 (particle diameter range of 38-75 µm) at a superficial linear velocity of 1.75 cm/sec. This linear velocity was achieved using sorbent tubes with 11 mm internal diameter; the outer diameter of such tubes was compatible with standard 1/2" fittings. Laboratory studies detailed here used gas chromatography with both flame ionization detection (GC/FID) and electron capture detection (GC/ECD) for detection and quantification.

Field-collected samples showed that neutral species such as aliphatic and aromatic hydrocarbons were retained by this sorbent in addition to the phenolic and acidic species. For this reason, extraction methods were developed for selective extraction of neutral species prior to extraction of phenols. These methods were developed for neutral specie levels 1000 times greater than anticipated phenol levels and resulted in greater than 90% recovery of spiked neutral species.

Limited studies carried out to assess the stability of two reactive phenols, phenol and 3-CH_3-phenol, indicated that these phenols are not adversely affected by (1) long term storage (1 month) at ambient temperature or (2) exposure during sampling to high ambient levels of nitric acid (6 ppb). Recoveries in these experiments were similar to control experiments; mono-nitrated analogs of these phenols were not detected in the sorbent extracts.

Field sampling with the AG MP-1 sorbent was carried out at two locations in the northern Delaware area and at three locations in the Columbus, Ohio area. Analyses of field-collected samples were performed using gas chromatography/mass spectrometry with electron impact ionization (EI GC/MS) and methane negative chemical ionization (NCI GC/MS). With exception of four samples collected in Delaware on 8/3/89, all sorbent samplers used in Delaware were preceded by muffled glass fiber filters which appeared to retain significant quantities of several phenols. For this reason, most conclusions of ambient levels were limited to the samples collected without filters. Three native phenols were detected and quantified in the Delaware-collected samples at levels of 0.6-60 $\mu g/m^3$. Because confirmatory information is not available regarding the phenol levels at the sites sampled, the feasibility of this sorbent collection method can only be inferred from (1) recoveries of the deuterated compounds spiked to the sorbent prior to sampling and prior to laboratory extraction and (2) relative levels of native analytes in lab blanks, field blanks, sector samples (passive samplers) and co-located samples collected at two different sampling rates.

For the entire set of samples collected in the Delaware area, deuterated compound recoveries were variable, 20-96%. Difficulties in extracting the non-polar end of these compounds from the polymer backbone, combined with evaporative losses encountered during an additional concentration step, appeared to be the factors responsible for the low recoveries. For sorbent sampling in the Columbus area, recoveries of the deuterated compounds were more consistent with laboratory results due to appropriate changes in the extraction protocol. Recoveries of deuterated compounds in those samples were 60-120%. In future studies, quantification with GC/MS may be improved by the use of a phenolic, rather than neutral, internal standard; such a change would likely prevent quantified recoveries greater than 100%.

For the subset of Delaware samples collected on 8/3/89, the sorbent tube used as a passive sampler contained native phenol levels similar to the levels obtained with the sorbents sampled at 20 and 100 mL/min. These results indicated that this sorbent material may be used effectively in passive samplers of proper design. Lab blanks showed minimal levels of one analyte (phenol) detected in field samples. The field blank contained relatively high levels of phenol and one other phenolic analyte, 3- and/or 4-OH-benzaldehyde; except for phenol, calculated ambient levels for the native analytes were greater than the field blank levels, indicating that these analytes are indeed present at significant levels. Some channeling of the air stream through the sorbent may have occurred; although higher quantities of each analyte were collected at the 100 mL/min sampling rate (relative to the 20 mL/min sampling rate), the calculated ambient concentrations were significantly higher from data obtained with the sorbent at the 20 mL/min sampling rate. Because significant losses also occurred during the final solvent concentration step used for these samples, differences in calculated ambient concentrations may not be valid for assessing collection efficiency of the sorbent.

The sample collected in the Battelle parking lot, reflecting primarily automotive emissions, was analyzed for tentative identification of those compound classes which may be collected in urban atmospheres by AG MP-1. Aliphatic carboxylic acids and alkyl-phenols were the dominant species detected using EI GC/MS. The NCI GC/MS analysis, which provided selective and sensitive detection of electronegative compounds, produced numerous spectra suggestive of hydroxylated nitro-aromatic (OH-NO_2-) compounds. The spectrum of one compound suggests OH-diNO_2-substitution of the azaarene cinnoline. Given the enhanced carcinogenicity of azaarenes relative to the corresponding PAH, the enhanced mutagenicity of diNO_2-PAH relative to NO_2-PAH, and the enhanced bioavailability of OH-NO_2-PAH relative to NO_2-PAH, a compound such as this tentatively identified OH-NO_2-azaarene merits further investigation. Tentative identification of this OH-diNO_2-cinnoline represents the first reporting of a OH-diNO_2-aromatic compound in an environmental sample.

Analyses of the Delaware-collected samples suggest that for the environments sampled, chloro-, nitro- and methyl-phenol levels were less than 1 ppbv. Because greater sensitivity for detection and quantification of volatile phenols, with possible exception of pentachlorophenol, cannot be achieved by concentrating the sorbent extract to analysis volumes less than 1 mL, increasing the volume of air sampled is the logical alternative. Sampling at 1 L/min through sorbent beds of 5 cm diameter and 2-4 cm bed depth would provide the same linear sampling velocity used here and, presumably, the same collection efficiencies.

The particular sites chosen for these field evaluations probably do not contain high ambient levels of phenols. More appropriate sites for sampling might include those with high pollutant levels from automotive and/or diesel emissions, coal combustion and/or coking operations, oil refining, pulp and paper mill operations, chloro-phenol production, residential wood combustion, and sewage aeration operations.

SECTION 3
RECOMMENDATIONS

Based on the results of this study, sampling at 100 mL/min for vapor phase phenols may be applied best to air heavily impacted by specific emission/pollution sources. The method evaluated here may not provide sufficient sensitivity for ambient levels less than 1 ppbv. Therefore, the recommendations listed here are divided into two categories, those specific to the further evaluation and development of the sorbent sampler described here and those specific to development of a similar AG MP-1 based sampler compatible with higher sampling rates.

We recommend further study of the following areas related to the sorbent sampler discussed in this report:

- Evaluation of the retention of vapor phase phenols by acid-washed glass fiber and quartz fiber filters.
- Evaluation of the components of laboratory AG MP-1 method blanks, with particular emphasis on phenolic and acidic species. The variability in concentration for such analytes needs to be determined before and after sampling (12-24 hr at 100 mL/min with zero air); in addition, those neutral compounds which are purged from the sorbent and those neutral and/or phenolic compounds which are retained need to be identified. These analyses should be performed by GC/MS.
- Evaluation of extraction procedures which ensure complete recovery of phenolic/acidic analytes following extended (12-24 hr) sampling periods at 100 mL/min.
- Evaluation of the collection efficiency of AG MP-1 sorbent for phenols from dilute (~ 1 ppbv) gas streams. For these studies, phenols should be delivered to the dilution chamber and sorbent continuously over 12-24 hr, rather than the 1-2 min used and reported here.
- Further evaluation of stability of phenols and extraction efficiency from AG MP-1 following storage. In particular, studies

need to address time dependency of any trends, with analyses of multiple samples containing diverse types of phenols.

- Further evaluation of stability of phenols toward ambient levels of nitrating gases. In particular, studies are needed wherein spiked analytes are exposed to complex atmospheres which more closely simulate true ambient conditions. Analyses of exposed sorbents in such studies should be carried out using GC/MS, rather than GC, analysis methods.

We recommend additional studies to determine the range of applications for ambient sampling with AG MP-1:

- Development of an AG MP-1 based sorbent sampler for operation at 1-2 L/min. A sorbent bed 5 cm in diameter and 2-3 cm in depth should provide phenol collection efficiencies equivalent to those determined here.

- Development of an AG MP-1 based sorbent sampler for operation at 10-100 L/min. Measurement of breakthrough and/or collection at lower sampling rates than these with relatively small sorbent quantities should provide the necessary information for estimating the sorbent quantity needed for quantitative collection at the faster sampling rates.

- Development of an AG MP-1 based passive sampler with nominal sampling rate of 80-100 mL/min.

- Evaluation of the anion exchange membrane AG 1-X8 (available from Bio-Rad; 90% AG 1, chemically similar to AG MP-1, incorporated into a polytetrafluoroethylene matrix) as an inlet filter on canisters or Tenax samplers. This membrane might effectively remove those more polar ambient species which are not removed during the analysis and/or cleanup steps.

- Evaluation of the anion exchange membrane AG 1-X8 as the inner surface of an anular denuder. The porosity and styrene-divinylbenzene backbone of the sorbent may enhance the collection efficiency of this matrix for organic acids and phenols relative to a conventional NaOH or Na_2CO_3 denuder surface: sorption by the matrix backbone should improve the capture efficiency of the exchange sites for organic acids and phenols relative to strong acids such as HNO_3 and SO_2. This retention should result in better performance of a denuder than could be achieved using a simple NaOH coating.

SECTION 4
EXPERIMENTAL METHODS

4.1 Preparation and Storage of Standard Analyte Mixtures

The source and purity of analytes used for this program are listed in Table 4.1 by task or purpose. The list includes the 14 hydroxylated and phenolic analytes and 2 internal standards (for quantification) used for the laboratory evaluations of this program. The 3,4-dimethylphenol was used as internal standard for the GC/FID analyses and dibromooctafluorobiphenyl (DBOB) was used as internal standard for the GC/ECD analyses. Phenol and 3-methylphenol were used to assess both storage stability and stability toward a simulated atmosphere containing HNO_3. The 7 neutral interference compounds selected for this program were aliphatic, aromatic or aromatic ketone compounds. These compounds were analyzed using GC/FID; quantification was performed by external calibration, and thus internal standards were not used. Deuterated phenolic compounds were used as recovery standards for field-collected samples. These analytes were spiked to the AG MP-1 either prior to sampling (field recovery) or prior to extraction (lab recovery). Perdeuterated naphthalene was added as internal standard for the GC/MS analyses of the field-collected samples.

A stock solution of each analyte was prepared at 5 mg/mL in methyl-t-butyl ether (MTBE) in a 4 dram vial which had been precleaned at high temperature (muffle furnace at 400 °C) and silylated in vacuo at 190 °C with hexamethyldisilazane. Mixtures of analytes were prepared as dilutions of these stock solutions.

For GC/FID analyses, 25 mL calibration mixtures of the 14 analytes were prepared from the stock solutions at concentrations of 100, 60, 30, 10, 6, 3, 1, and 0.6 µg/mL (ng/µL); the GC/FID internal standard was added to each calibration solution at the 10 ng/µL level. Each calibration mixture was divided among 25 GC analysis vials (1.8 mL volume; cleaned and silylated per above); vials were sealed with crimp-top caps and stored at -20 °C until needed for analysis.

To deliver 1, 10, and 100 µg quantities of the 14 phenols as spikes, mixtures of these phenols were prepared at concentrations of 2, 20 and 200 µg/mL. GC analysis vials (screw-capped, 1.8 mL volume; cleaned and silylated per above) were filled headspace-free with the spiking solutions and stored at -20 °C until needed. Each vial was opened only once, providing material for the three replicate spikes (500 µL each) of a single experiment. In this way, loss of more volatile analytes through vaporization and/or concentration of the less volatile species through vaporization of solvent were minimized. After spiking, the remaining solution of each vial was discarded.

To deliver low, medium and high quantities (see Table 4.2 for definition of the levels, e.g. 10/1 mg) of the interference compounds as spikes, mixtures of these analytes were prepared at low (0.2/0.02 mg/mL), medium (2/0.2 mg/mL) and high (20/2 mg/mL) levels. The highest spike level represented analyte levels either 10 or 100 times greater than the highest phenol spike quantity. GC analysis vials (screw-capped, 1.8 mL volume; cleaned and silylated per above) were filled headspace-free with the spiking solutions and stored at -20 °C until needed. Each vial of interference spiking solution provided material for the 3 replicate spikes of a single experiment. Calibration solutions for quantification were prepared at the following levels: 1/0.1, 5/0.5, 10/1, 50/5, 100/10, 500/50, 1000/100 µg/mL (or ng/µL). The 25 mL volume of each calibration solution was divided by 1 mL aliquots into GC vials (crimp top cap, 1.8 mL volume; cleaned and silylated) which were then sealed and stored at -20 °C until used. The two standards at highest concentration levels, 500/50 and 1000/100 ng/µL, were analyzed only for data points in the quantification curves of the analytes at the 50 and 100 ng/µL levels; detector signals for the compounds at the 500 and 1000 ng/µL levels were either non-linear or saturated.

4.2 Activation and Storage of Resin

Fifty grams of AG MP-1 sorbent, obtained from Bio-Rad with Cl^- as counterion, was treated initially with methanolic HCl to clean the sorbent and assure that all exchange sites had Cl^- as counter ion. The counterion was then converted to OH^- with aqueous NaOH and the sorbent was extracted in sequence with solvents listed in Table 4.3. The sorbents of mesh sizes 20-50, 50-100 and 100-200 were extracted in 2 L beakers; with each activation/extraction solvent, the sorbent was allowed to settle for approximately 5 min and then the solvent was decanted. The sorbent of mesh size 200-400 was divided into four equal portions and each was activated and extracted in a 500 mL centrifuge tube; with each activation or extraction solvent, the tube was centrifuged for 20 min at 1750 rpm to separate solvent and sorbent. The pH of the millipore water rinses was checked, as indicated in Table 4.3, to verify removal of acid and base. The sorbent was stored under a layer of MTBE until used.

4.3 Analysis Methods

4.3.1 GC/FID for Phenols: For laboratory experiments in which 100 µg quantities of phenols were spiked, gas chromatography with flame ionization detector (GC/FID) was used for detection and analysis of all analytes. Quantification was obtained by comparison of analyte response relative to the internal standard, 3,4-diCH_3-phenol. For laboratory experiments in which 10 and 1 µg quantities of phenols were spiked, GC/FID was used for the analysis of all analytes except 2-NO_2-, 3-NO_2-, 6-CH_3-2-NO_2-, 2,4-diCl- and pentaCl-phenol. Although the three NO_2-phenols were detected and could be quantified by GC/FID at these lower levels, values obtained by GC/ECD, as described later, appeared less variable. The GC/FID analysis conditions are given in Table 4.4.

4.3.2 GC/ECD for Phenols: For the analysis of the above named nitro- and chloro-phenols, the gas chromatography with electron capture detector (GC/ECD) analysis was preceded by methylation with diazomethane as described. To the final 1 mL extract of 10 µg phenol-spiked samples, 5 µg of dibromooctafluorobiphenyl (DBOB; 10 µL of a 500 ng/µL solution) was added (in addition to 10 µg of 3,4-diCH_3-phenol). A 20 µL portion of the extract was transferred to a 1.8 mL GC vial for methylation. To the final 1 mL extract of 1 µg phenol-spiked samples, 0.5 µg of DBOB (10 µL of a 50 ng/µL solution) was added (in addition to 10 µg of 3,4-diCH_3-phenol); a 200 µL portion of the extract was transferred to a 1.8 mL GC vial for methylation. To the 20 µL aliquot, 180 µL of MTBE and 800 µL of 6.25:93.25 methanol:mtbe (v:v) were added. To the 200 µL aliquot, 800 µL of the above methanol:MTBE solution was added. With each set of samples prepared for GC/ECD analysis, duplicate calibration standards at analyte concentrations of 0.2, 0.1, 0.05 and 0.0 ng/µL were prepared in GC vials and methylated simultaneously with samples. Freshly-prepared GC/ECD standards were used each time to verify correct methylation of samples. Analyte and solvent quantities used in the preparation of the GC/ECD standards are given in Table 4.5.

Schematic representation of the diazomethane generator is shown in Figure 4.1. Each standard or extract was methylated for approximately 20 sec. After introduction of the diazomethane, solutions were held for 30 min; during that time, solutions were checked for retention of yellow color to verify that excess diazomethane remained available for complete reaction. After the hold period, the solutions were purged with a gentle stream of dry nitrogen to remove the excess diazomethane; solvent volumes were then adjusted to 1 mL with MTBE if necessary. The GC/ECD analysis conditions are similar to those for the GC/FID analyses. The differences are included in Table 4.4.

4.3.3 GC/FID for Neutral Interference Compounds: For GC/FID analyses of the 7 neutral interference compounds, each sorbent extract was adjusted to a 10 mL volume and 1 mL was transferred to a GC vial for analysis. In addition, for extracts where the sorbent had been spiked with the high level of interference compounds, a 100 µL aliquot of sorbent extract was diluted to 1 mL with MTBE, and that diluted solution was analyzed by GC/FID also. As listed in Table 4.6, sorbent extracts of the low level interference spikes were quantified using a three point calibration curve representing 10, 50, and 100% recovery. Sorbent extracts of the medium level interference spikes were quantified using a five point calibration curve representing 1, 5, 10, 50 and 100% recovery. Analysis of the initial 10 mL extract of high level interference spiked-sorbent provided quantification of analytes spiked at the 10 mg level whose recoveries were ≤ 10%, and quantification of analytes spiked at the 1 mg level. Analysis of the diluted (10:1) extract of the high level spiked-sorbent was used to obtain quantification of those 10 mg-spiked analytes whose recoveries were 10-100%. For extracts of 10 mg-spiked sorbents, calibration solutions which represented 0.1, 0.5, 1, 5, and 10%

recovery for the initial extract represented 1, 5, 10, 50 and 100% recovery for the diluted extract.

For a MTBE extract of sorbent, no adjustment in solvent was necessary. For a methanol extract, the solution was concentrated to 5 mL under dry nitrogen and then brought back to the 10 mL volume with MTBE prior to analysis. The GC/FID analysis conditions for these analytes are identical to those given for the GC/FID analyses of the phenols (Table 4.4).

4.3.4 GC and GC/MS of Field-Collected Samples: Each AG MP-1 sorbent used for field collection of vapor-phase phenols was spiked with two different sets of representative deuterated compounds: one set prior to field sampling (field recovery) and the other set prior to sample extraction (lab recovery). The spike levels of the deuterated compounds are given in Table 4.7. Spike levels are listed there for samples collected by the Project Officer in Delaware and samples collected by Battelle personnel in Columbus.

The final 1 mL sorbent extract of each Delaware-collected field sample was transferred to a 2 mL graduated Chromaflex tube (Kontes Glass Co.; cleaned and silylated) and then split for GC/ECD and GC/MS analyses after addition of 0.5 μg of DBOB. A 200 μL aliquot was removed, methylated (as described in Section 4.3.2) and analyzed using the GC/ECD conditions listed in Section 4.3.2. The 800 μL volume of three field samples was analyzed using EI GC/MS for quantification (external calibration) of the field recovery deuterated compounds. In these analyses the area of each analyte's base peak was used for quantification. These three samples and all others were slowly concentrated under a stream of dry nitrogen to 80 μL. Perdeuterated naphthalene (0.8 μg) was added to each extract to give a final naphthalene-d_8 concentration of 10 ng/μL. Each extract was analyzed by EI GC/MS for quantification of low level analytes, the lab recovery deuterated compounds, and the field recovery deuterated compounds for a second time. Quantification was performed using the internal standard method. Lab recovery deuterated compounds were quantified using the area of each compound's base peak. Field recovery compounds were quantified using the area of a fragment ion whose intensity was 10-40% of the base peak, as the response for the base peak was now saturated.

The samples collected in Columbus, Ohio at the municipal bus garage and municipal composting facility were concentrated to 1 mL; naphthalene-d_8 was added to give final concentration of 10 ng/µL. Due to similarity of spike levels of field and lab deuterated recovery compounds, a single analysis by EI GC/MS was used for quantification of these analytes. The sample collected in the Battelle parking lot (Columbus, Ohio) was concentrated to 1 mL by Kuderna-Danish (K-D) concentration and then to ~20 µL by N_2 evaporation. Deuterated recovery standards were not added to the sorbent; an internal standard was not added to the extract. Quantification of analytes was not performed; qualitative identification of components, based upon EI and NCI mass spectra and retention times of authentic standards, was the purpose of these analyses. The EI and NCI GC/MS analysis conditions are listed in Table 4.8.

Standard mixtures of 29 phenolic and carboxylic acid compounds were prepared at levels of 50, 20, 10, 2, and 0.5 ng/µL for the GC/MS quantification of Delaware samples. The components of these mixtures are listed in Table 4.9.

4.4 Extraction of Phenols from Acidic Methanol:MTBE

4.4.1 Extraction without additional MTBE (Method 1): The acidic solution used to extract phenolic analytes from 1 gram of AG MP-1, 10 mL of conc HCl (2% by volume) in 15:85 methanol:MTBE (v:v), was placed in a 60 mL separatory funnel. Each acidic solution was spiked with 500 µl of a MTBE solution containing either 1, 10 or 100 µg quantities of the 14 laboratory evaluation phenolic analytes; triplicate experiments plus a blank were prepared at each spike level. After addition of 15 mL of a 15% (by weight) aqueous NaCl solution, the mixture was shaken for 2 min. The aqueous layer was removed, a 5 mL aliquot of the aqueous NaCl solution was added, and the mixture was shaken for 2 min. After the second aqueous layer was removed, the organic layer was rinsed through a 25 mL chromatography column containing ~1 gram Na_2SO_4 (for removal of residual water) into a 25 mL K-D evaporator tube. The eluate was concentrated to ~1.5 mL by K-D evaporation and then to a final 1 mL under a gentle stream of dry N_2. The GC/FID internal standard, 3,4-diCH_3-phenol, was added and the solution was analyzed as described in Section 4.3.1.

4.4.2 Extraction with additional MTBE (Method 2): The experiment described in Section 4.4.1 was repeated with the exception that 7 mL of additional MTBE was added to each separatory funnel for extraction. This modification was made to provide an extraction volume of MTBE equivalent to the initial volume of aqueous solution used. This experiment was performed in triplicate with 1 blank using the 100 µg spike quantity of phenols. This extraction procedure was used for all laboratory evaluation studies of vapor spiking and for all field-collected samples.

4.5 Extraction of Phenols from AG MP-1

4.5.1 Extraction after Solvent Spike to Solvent-Slurried AG MP-1: Approximately 1 g of 20-50 mesh AG MP-1 was transferred as an MTBE slurry to an open chromatography column (10 mm i.d. x 20 cm length, Fischer-Porter Glass, Inc.). After the AG MP-1 had settled to the bottom of the column, a 10 mL aliquot of MTBE was added to each column; the top of the solvent layer was approximately 10 cm above the top of the AG MP-1. The top of the MTBE solvent layer was spiked with 500 µL of a solution containing either 1, 10 or 100 µg quantities of the 14 laboratory evaluation phenols. The MTBE was slowly drained through the AG MP-1 and collected in a 15 mL conical centrifuge tube. A 10 mL aliquot of the acidic methanol:MTBE solution was added to the column and allowed to slowly drain through the AG MP-1 into a 60 mL separatory funnel. The phenols in this acidic eluent were extracted back into neutral solvent (MTBE) using the method described in Section 4.4.1 and analyzed by GC/FID and GC/ECD as described in Sections 4.3.1 and 4.3.2. The initial MTBE eluate of the column was concentrated to 1 mL and analyzed using GC/FID.

The experiment described above was repeated with the exception that extraction of the phenols from the acidified methanol:MTBE eluate was carried out using the modified method of Section 4.4.2. This experiment was performed using only the 100 µg quantities of phenols. These two experiments were performed in triplicate at each spike level, with a method blank at each level.

4.5.2 Extraction after Solvent Spike to Dry AG MP-1: The 200-400 mesh AG MP-1 was dried thoroughly and placed in sorbent tubes between silanized glass wool plugs. Approximately 1 g of AG MP-1 was placed in each tube. The phenolic analytes and interference compounds were spiked as MTBE solutions into the center of the sorbent using a syringe. For some experiments, extraction followed directly after spiking. For other experiments, the sorbent tube was dried by a He purge of the sorbent tube for 20 min at 100 mL/min and 55 °C. To accomplish this purge, the sorbent tube was connected to the exit end of a GC injector; the GC oven was held at 50 °C to ensure volatilization of the MTBE.

For extraction of phenols from AG MP-1, several methods were evaluated. For several spiked sorbent tubes, the tube was placed in a vertical position and connected to a small piston pump (FMI Lab Pump, Model RP-G150) using 1/8" Teflon tubing. The solvents used to elute the sorbent were introduced at the bottom of the sorbent tube and forced upward through the sorbent bed at a flow rate of 0.1 mL/min. When air bubbles and voids appeared in the sorbent bed, a vibrating engraving tool was used to agitate the bed and release the pockets of air. After this extraction, the AG MP-1 was transferred from the tube to a 15 mL vortex tube; the sorbent was extracted a second time with acidic methanol:MTBE using vortex action. This sorbent eluate was removed by pipet. For other spiked sorbent tubes, the sorbent was transferred after spiking and drying to a 15 mL vortex tube. After addition of solvent, the tube was vortexed for ~1-2 min; the sorbent eluate was removed by pipet. The sorbent was rinsed twice with 3.5 mL of MTBE and each rinsate was added to the separatory funnel. For these experiments, extraction of the phenols from the acidic solution into neutral MTBE was carried out as described in Section 4.4.2.

4.5.3 Extraction after Vapor Spike to Dry AG MP-1: Phenols that were spiked from the vapor-phase under laboratory conditions to 7 mm i.d. tubes containing 1 g of 20-50 mesh or 50-100 mesh AG MP-1 were extracted from the AG MP-1 in 50 mL beakers. The spiked sorbent and silylated glass wool plugs from either end of the sorbent bed were pushed into the beaker with a glass stirring rod. The acidified methanol:MTBE was added to this beaker of sorbent, which was then mixed for ~2 min. The eluate of the sorbent was transferred by pipet to the separatory funnel. The sorbent was rinsed twice with 3.5 mL of MTBE and each rinsate was added to the separatory funnel. Extraction of phenols from the acidic solution was carried out as described in Section 4.4.2.

Phenols that were spiked from the vapor-phase under laboratory conditions to 7 mm i.d. tubes of 1 g of 100-200 mesh or 200-400 mesh AG MP-1 were extracted from the AG MP-1 in 15 mL conical centrifuge tubes. The spiked sorbent and silylated glass wool end plugs were pushed into a centrifuge tube, the neck opening of which being slightly larger than the o.d. of the sorbent tube. The first 2 mL of the acidified methanol:MTBE eluant was used to rinse the walls of the sorbent tube. This eluate and the remaining acidic solvent were added to the AG MP-1. Phenols were extracted from the sorbent by vortex action, for ~1 min. The centrifuge tube was then centrifuged for ~10 min to separate resin from solvent. Sorbent was rinsed twice with ~4 mL of MTBE and each rinsate was added to the separatory funnel. Phenols were extracted from the acidified solution into MTBE as described in Section 4.4.2.

Phenols that were spiked from the vapor-phase under laboratory conditions to 11 mm i.d. tubes of 1 g of 200-400 mesh AG MP-1 were extracted from the AG MP-1 in 6 dram (~25 mL) flat-bottom vials. The spiked sorbent and silylated glass wool end plugs were pushed into the vial. An initial 2 mL aliquot of the acidified methanol:MTBE was used to rinse the tube walls; the remaining 8 mL was added directly to the sorbent. Phenols were extracted by vortex action, for ~1 min. The vial was centrifuged for ~10 min to separate resin and solvent. Sorbent was rinsed as above. Phenols were extracted from the acidified solution as described in Section 4.4.2. All experiments described here were performed in triplicate with a method blank.

The method described above was used for the extraction of field-collected phenols. For extraction of sorbent used in sampling air at the municipal bus garage and composting facility, 50 mL round-bottom centrifuge tubes were used to obtain better vortex action, and presumably better contact of sorbent with acidic solution. The extraction procedure used in these experiments was identical to that described above, with the exception of the extraction vessel.

4.5.4 Combination of the Two Extraction Procedures: In anticipation of extracting phenols from larger sorbent quantities (> 1 g, as would be expected for 1 to 4 L/min sampling rates), the following method was evaluated. This procedure combined extraction of the phenols from the AG MP-1 and extraction of the phenols from acidic solution into neutral solvent. Approximately 1 g of dry 200-400 mesh AG MP-1 and two plugs of silylated glass wool were placed in a 50 mL centrifuge tube. The sorbent was spiked with 500 µL of a solution containing 1 µg each of the 14 laboratory evaluation phenols. After the solvent was dispersed, 10 mL of MTBE and 10 mL of 2% aqueous conc HCl were added and the tube was mixed by vortex action for ~1 min. The tube was centrifuged for 10 min to separate sorbent and solvent and the organic layer was removed by pipet. This organic extract was filtered through ~1 g of Na_2SO_4 into a K-D concentrator tube. The centrifuge tube, containing sorbent and aqueous acid, was rinsed two additional times with 10 mL of MTBE; these extracts were filtered through Na_2SO_4 added to the K-D tube. After concentration to 1 mL, the GC/FID internal standard was added and the extract was analyzed by GC/FID as described in Section 4.3.1. This experiment was performed in triplicate with a method blank.

4.6 Extraction of Neutral Interference Compounds from AG MP-1

4.6.1 Extraction after Solvent Spike to Solvent-Slurried AG MP-1: Experiments to evaluate removal of neutral compounds from AG MP-1 were very similar to experiments described in Section 4.5 for the phenols. As described in Section 4.5.1, approximately 1 g of either 20-50 or 200-400 mesh AG MP-1 was placed as a MTBE slurry in an open chromatography column. Interference compounds were spiked at the three different levels (see Table 4.2) to the top of the solvent layer and eluted in sequence with two or three 10 mL aliquots of MTBE and two 10 mL aliquots of methanol. The eluates were collected separately and analyzed separately to determine elution profiles of the neutral analytes. All experiments were performed in triplicate with a method blank.

4.6.2 Extraction after Solvent Spike to Dry 200-400 mesh AG MP-1: The neutral compounds were spiked as MTBE solutions to dry 200-400 mesh AG MP-1 which had been placed in sorbent tubes. For the neutral compounds spiked to AG MP-1 in 7 mm i.d. tubes, extractions were identical to methods used for extraction of the phenols (Section 4.5.2) as both phenols and interference compounds were spiked to the sorbent tubes.

In addition to those experiments, neutral compounds were spiked as MTBE solution to dry AG MP-1 (1 g) in 11 mm i.d. sorbent tubes. The AG MP-1 was transferred to either a flat-bottom 6 dram (~25 mL) vial or a 50 mL round-bottom centrifuge tube. AG MP-1 in the 6 dram vials was extracted using either vortex action or sonication; AG MP-1 in the centrifuge tube was extracted using vortex action. The same sequence of extraction solvents was applied in all experiments: three 10 mL aliquots of MTBE followed by two 10 mL aliquots of methanol. These latter experiments were performed in duplicate.

4.7 Method for Vapor Spike and Simulated Sampling of Phenols

4.7.1 Preparation of Sorbent Tubes: Tubes of two different internal diameters were evaluated for the collection of vapor-phase phenols: 7 mm i.d and 11 mm i.d. Both tubes were approximately 10 cm in length; the 1 g sorbent bed was approximately 5 cm in length in the 7 mm i.d. tube and approximately 3.5 cm in length in the 11 mm i.d. tube. At 100 mL/min sampling rate, superficial linear velocity (face velocity) was 4.3 cm/sec through the 7 mm i.d. tube and 1.75 cm/sec through the 11 mm i.d. tube.

The AG MP-1 used for simulated sampling of vapor-phase phenols was dried under a stream of dry N_2 until all visible solvent was removed and the sorbent was free-flowing. Silanized glass wool plugs, ~1 cm in length, were used to retain the 1 g of AG MP-1 in the tubes. After initial experiments for simulated sampling of vapor-phase phenols with 200-400 mesh AG MP-1 at 100 mL/min sampling rate, an additional drying period was instituted prior to sampling. To accomplish this additional drying, sorbent tubes were filled with AG MP-1 as described in Section 4.7.1 and then subjected to a 15-20 min purge of He gas at 100 mL/min at

55 °C; the front end of the sorbent tube was connected to the exit end of the GC injector. After this drying period, the side walls of the tube were agitated with a vibrating engraving tool to compact the sorbent. The sorbent tube was weighed before addition of AG MP-1 and after completion of drying to obtain sorbent mass.

4.7.2 Laboratory Simulation of Vapor Phase Sampling: Both 7 and 11 mm i.d. sorbent tubes, containing 1 g of AG MP-1, were connected to the exit end of an HP 5730 GC packed column injector. A non-standard glass injection liner was used; the liner extended beyond the injector into either a dilution chamber or the front end of a sorbent tube. In earliest simulated sampling experiments, a dilution chamber (5 mm i.d. x 10 cm length) was used to provide mixing of analytes with He prior to contact with the sorbent. Dilution chambers of Teflon and nickel were used. A schematic representation of the injection system used to simulate vapor phase collection is shown in Figure 4.2.

The 1, 10, and 100 µg quantities of laboratory evaluation phenols were spiked as a 500 µL MTBE solution into the He carrier gas of the injector. The injector was held at 250-300 °C; the GC oven was held at 50-55 °C to prevent condensation of MTBE. The GC flow rate (simulated sampling rate) was maintained at either 10, 20, or 100 mL/min by the GC flow controller. Injection of analytes was made over a relatively short period of time, 1-2 min. Following injection, an additional 15 min He purge of the sorbent was made at the flow rate used for sampling.

4.8 Method of Evaluating Stability of Sorbent-Bound Phenols

4.8.1 Stability During One Month Storage: Four 7 mm i.d. sorbent tubes, each containing 1 g of 200-400 mesh AG MP-1, were prepared as described in Section 4.7.1. Two tubes were spiked with 500 µL solutions containing 100 µg quantities of phenol and 3-CH_3-phenol; the other two tubes received no spike. Solvent in each sorbent tube was removed by subjecting the sorbent to a flow of He at 100 mL/min for 5 min. Sorbent tubes were fitted with plastic end caps and held at room temperature for one month, then extracted (Section 4.5.3) and analyzed by GC/FID (Section 4.3.1).

4.8.2 Stability Toward HNO_3: Two 7 mm i.d. sorbent tubes and two 11 mm i.d. sorbent tubes, each containing 1 g of 200-400 mesh AG MP-1, were prepared as described in Section 4.7.1. One tube of each i.d. was spiked with a 500 µL solution containing 100 µg quantities of phenol and 3-CH_3-phenol; analytes were not added to the other two tubes. Solvent in the sorbent was removed by a He purge at 100 mL/min. After removal of solvent, the front end of each sorbent tube was connected to a sampling port on Battelle's 17,300 L environmental chamber. The chamber was charged with ADDCO air to which was added HNO_3 from a warm watch-glass. Concentration of the HNO_3 was monitored during the 8 hr experiment using the Sciex TAGA atmospheric pressure ionization mass spectrometer, which was connected directly to the environmental chamber. Concentration of HNO_3 averaged 6 ppbv (5.0-7.8 ppb) during the experiment. The Distributed Air Volume Sampler (DAVS) was used to draw chamber air simultaneously through each sorbent tube at 100 mL/min for 8 hr.

At the completion of sampling, sorbent tubes were extracted (Section 4.5.3) and concentrated to 1 mL final volume. A 200 µL aliquot of each extract was methylated and analyzed using GC/ECD (Section 4.3.2) for detection of ortho and para mono-nitration products: 2-NO_2-phenol, 4-NO_2-phenol, 3-CH_3-2-NO_2-phenol, 3-CH_3-4-NO_2-phenol, and 3-CH_3-6-NO_2-phenol. The remaining 800 µL volume was analyzed using GC/FID (Section 4.3.1) for quantification of the originally-spiked phenol analytes.

4.9 Collection of Field Samples

4.9.1 Preparation of Sorbent Tubes: The sorbent preparation procedure described in Section 4.7.1 was used for the preparation of sorbent for field collection of phenols. An additional preparation step was added to the procedure when preparing the final sorbent tube for the program (that being the sorbent used for sampling at the Columbus composting facility). After drying the sorbent with the He gas stream, the sorbent was removed from the tube to a 6 dram vial and shaken vigorously to obtain a free-flowing powder (AG MP-1 formed well-packed clumps when dried in the sorbent tube). The free-flowing powder was then placed in the sorbent tube; the bed was compacted using the vibrating engraving tool. After packing, deuterated recovery standards were added to all sorbents, as described in Section 4.3.4, except the sample used for ambient air collection in the Battelle parking lot.

A 7 mm i.d. sorbent tube containing 200-400 mesh AG MP-1 was used for collection of phenols in the Battelle parking lot. The 11 mm i.d. sorbent tubes containing 200-400 mesh AG MP-1 were used for field collection of phenols at the Pigeon Point (PP) and Rifle Range (RR) areas of Delaware. The latter sorbent tubes were shipped to the field by overnight carrier at ambient temperature. Additional sorbent tubes of 200-400 mesh AG MP-1 in 11 mm i.d. tubes were used for sampling ambient air at the municipal bus garage and municipal composting facility in Columbus.

4.9.2 Collection of Samples: Muffled glass fiber filters preceded the sorbent tubes for sampling carried out in the Battelle parking lot and the two Delaware sites. One exception here were the four Delaware samples collected on 8/3/89 at Pigeon Point. None of these sorbent tubes was preceded by a filter. In the Battelle parking lot, air was sampled at 60 mL/min for 40 hr using the DAVS. At the two Delaware sites, air was sampled at either 20 or 100 mL/min for 24 hr using the DAVS. At the municipal bus garage and composting facility in Columbus, air was sampled at 100 mL/min for 24 hr using three portable sampler pumps (Universal Flow Sample Pump, Model 224-PCXR7, SKC Corp.). The three pumps were arranged in series with each one providing sample collection for an 8 hr period.

Site selection and sampling/meterological data for the Delaware samples are not included here, as this information was collected by the Project Officer. The composting facility in Columbus was chosen to represent a site similar in waste handling operations to the Delaware Pigeon Point location.

4.9.3 Extraction and Analysis: Extraction of neutral compounds from sorbent was performed as described in Section 4.6.2; phenols were extracted as described in Section 4.5.3. Neutral compounds were extracted from the sorbent prior to extraction of phenols in the Battelle parking lot sample and all Delaware samples. Extraction of the sorbent with neutral solvent was not performed with the last samples collected in Columbus (bus garage and composting facility). For the municipal bus garage and composting facility samples, the sorbent was extracted twice in sequence with the acidified methanol:MTBE solvent. After extraction of analytes from acidified solution into neutral solvent, the two extracts of each sorbent were combined and analyzed as a single sample.

TABLE 4.1. SOURCE AND PURITY OF ANALYTES USED

Analyte		Source	Purity, %
Laboratory Evaluations			
Phenol		EPA-RTP	99.9
2-CH_3-phenol		Aldrich	98
4-CH_3-phenol		Chem Service	practical
2,3-diCH_3-phenol		Aldrich	97
2-Cl-phenol		Chem Service	not listed
4-Cl-phenol		Matheson Coleman and Bell	not listed
2,4-diCl-phenol		Eastman Organics	99
Penta Cl-phenol		Chem Service	not listed
2-NO_2-phenol		Eastman Organics	15% H_2O
3-NO_2-phenol		Aldrich	99
6-CH_3-2-NO_2-phenol		synthesized at Battelle 12/87	not determined
2-OH-benzaldehyde		Aldrich	98
2-OH-biphenyl		Aldrich	99
4-OH-indole		Aldrich	99
Laboratory Evaluation - Internal Standards for Quantification			
3,4-diCH_3-phenol	GC/FID	Chem Service	not listed
Dibromooctafluorobiphenyl	GC/ECD	Aldrich	99
Laboratory Stability Evaluations			
Phenol		EPA-RTP	99.9
3-CH_3-phenol		Chem Service	practical

TABLE 4.1. (Continued)

Analyte	Source	Purity, %
Laboratory Neutral Interference Evaluations		
Decane	Aldrich	99
Dodecane	Chemical Samples Co.	99
Tetradecane	Wiley Organics	99.5
o-Xylene	Chem Service	99
Biphenyl	EPA-RTP	99.9
Naphthalene	Aldrich	98
Fluorenone	Aldrich	98
Deuterated Recovery Compounds		
Field: Phenol-d_6	Aldrich	98
4-NO_2-phenol-d_4	MSD Isotopes	98.7
2,4-diCl-phenol-d_3	MSD Isotopes	98.9
Lab: 4-CH_3-phenol-d_5	MSD Isotopes	97.7
2-NO_2-phenol-d_4	MSD Isotopes	98.6
2-Cl-phenol-d_4	MSD Isotopes	98.5
Field Samples - Internal Standards for Quantification		
Naphthalene - d_8	Aldrich	98

TABLE 4.2. ANALYTE SPIKE LEVELS FOR NEUTRAL INTERFERENCE COMPOUNDS

Analyte	Nominal Spike Level					
	Low (0.1/0.01 mg)		Medium (1/0.1 mg)		High (10/1 mg)	
	Spiked Quantity, mg	Conc in Spike Soln, mg/mL	Spiked Quantity, mg	Conc in Spike Soln, mg/mL	Spiked Quantity, mg	Conc in Spike Soln, mg/mL
Decane	0.1	0.2	1	2	10	20
Dodecane	0.1	0.2	1	2	10	20
Tetradecane	0.1	0.2	1	2	10	20
o-Xylene	0.1	0.2	1	2	10	20
Naphthalene	0.01	0.02	0.1	0.2	1	2
Biphenyl	0.01	0.02	0.1	0.2	1	2
Fluorenone	0.01	0.02	0.1	0.2	1	2

TABLE 4.3. ACTIVATION AND EXTRACTION OF 50 g AG MP-1

Solvent	Volume, mL	Time, min	Number of Sequential Aliquots
6% conc HCl in methanol	250	10	1
Methanol	200	10	2
Millipore H_2O	450	10	2(a)
1 N NaOH	800	35	2
1 N NaOH	300	10	1(b)
Millipore H_2O	500	10	3(a,c)
Millipore H_2O:Methanol 1:1	500	10	1
Methanol	500	10	1
MTBE 500	10	1	

(a) Test for neutral pH before decanting final rinse.
(b) This step only for 200-400 mesh AG MP-1.
(c) 4-5 rinses necessary for 200-400 mesh AG MP-1 to give neutral pH.

TABLE 4.4. GC/FID AND GC/ECD ANALYSIS CONDITIONS

Parameter	
Column	DB-1701 (bonded 14% cyanopropylphenyl dimethyl siloxane)
Manufacturer	J and W Scientific
Length	30 M
Internal diameter	0.25 mm
Phase thickness	0.25 µm
Injector temp	250°C
Carrier Gas	He
Carrier Gas Linear Velocity	45 cm/sec
Temperature Program	60-250°C @ 8°C/min : GC/FID Analyses 60-250°C @ 4°C/min : GC/ECD Analyses
GC	Hewlett Packard 5890 : GC/FID Hewlett Packard 5730 : GC/ECD

TABLE 4.5. PREPARATION OF GC/ECD ANALYSIS STANDARDS

Analyte Conc ng/μL	Volume, μL			
	Analyte Mix at 1 ng/μL	MTBE	6.25 : 93.25 Methanol:MTBE	DBOB Stock at 50 ng/μL
0.2	200	0	800	2
0.1	100	100	800	2
0.05	50	150	800	2
0.00	0	200	800	2

TABLE 4.6. QUANTIFICATION OF NEUTRAL INTERFERENCE COMPOUNDS

	Nominal Spike Level			
	Low(a)	Medium(b)	High	
Analyte	Conc in 10 mL Representing 100% Recovery, µg/mL	Conc in 10 mL Representing 100% Recovery, µg/mL	Conc in 10 mL Representing 10/100% Recovery, µg/mL(c)	Conc in Effective 100 mL Representing 100% Recovery, µg/mL(d)
Decane	10	100	100	100
Dodecane	10	100	100	100
Tetradecane	10	100	100	100
o-Xylene	10	100	100	100
Naphthalene	1	10	100	-
Biphenyl	1	10	100	-
Fluorenone	1	10	100	-

(a) Three point calibration curve used for quantification represented 10, 50 and 100% recovery.

(b) Five point calibration curve used for quantification represented 1, 5, 10, 50 and 100% recovery.

(c) Five point calibration curve used for quantification represented 0.1, 0.5, 1, 5 and 10% recovery for first 4 analytes; seven point calibration curve used for quantification represented 0.1, 0.5, 1, 5, 10, 50 and 100% recovery for latter 3 analytes.

(d) Five point calibration curve used for quantification represented 1, 5, 10, 50 and 100% recovery for first 4 analytes; quantification of latter 3 analytes not necessary.

TABLE 4.7. QUANTITIES OF DEUTERATED SPIKE COMPOUNDS FOR FIELD-COLLECTED SAMPLES

Analyte	Spiked Quantity, µg
Field Recovery (Delaware and Columbus)	
Phenol-d_6	20
4-NO_2-phenol-d_4	20
2,4-diCl-phenol-d_3	20
Lab Recovery (Delaware)	
4-CH_3-phenol-d_5	0.4
2-NO_2-phenol-d_4	0.4
2-Cl-phenol-d_4	0.4
Lab Recovery (Columbus)	
4-CH_3-phenol-d_5	5
2-NO_2-phenol-d_4	5
2-Cl-phenol-d_4	5

TABLE 4.8. EI and NCI GC/MS ANALYSIS CONDITIONS

GC Parameter	
Column	DB-1701 (J and W Scientific)
Length	30 M
Internal diameter	0.25 mm
Phase thickness	0.25 μm
Injector temp	60°C (on column)
Carrier gas	CH_4
Linear velocity	60 cm/sec at 100°C
Temperature program	60°C for 1 min 60-280°C @ 6°C/min
MS Parameter	
Electron energy	70 eV : EI 150 eV : NCI
Source temp	200°C
Reagent gas	CH_4 : NCI
Reagent gas pressure	1 torr : NCI
Scan range	50-450 amu in 1.0 sec

TABLE 4.9. REFERENCE COMPOUNDS ANALYZED BY EI GC/MS

Compound	Source
Phenol	EPA-RPT
2-CH_3-phenol	Aldrich
4-CH_3-phenol	Chem Service
2,3-diCH_3-phenol	Aldrich
2,4-diCH_3-phenol	Eastman Organics
2,5-diCH_3-phenol	Aldrich
2,6-diCH_3-phenol	Chem Service
3,4-diCH_3-phenol	Chem Service
2-Cl-phenol	Chem Service
4-Cl-phenol	Matheson Coleman and Bell
2,4-diCl-phenol	Eastman Organics
2,6-diCl-phenol	U.S. EPA/RTP Repository
2,4,6-triCl-phenol	Chem Services
Penta Cl-phenol	Chem Services
2-NO_2-phenol	Eastman Organics
3-NO_2-phenol	Aldrich
4-NO_2-phenol	Aldrich
4-CH_3-2-NO_2-phenol	Aldrich
5-CH_3-2-NO_2-phenol	Aldrich
6-CH_3-2-NO_2-phenol	Synthesized at Battelle
2-CH_3-3-NO_2-phenol	Aldrich
4-CH_3-3-NO_2-phenol	Aldrich
6-CH_3-3-NO_2-phenol	Pfaltz and Bauer
2-CH_3-4-NO_2-phenol	Synthesized at Battelle
3-CH_3-4-NO_2-phenol	Aldrich
2-OH-biphenyl	Aldrich
2-OH-benzaldehyde	Aldrich
Hexanoic acid	Aldrich
Dodecanoic acid	Aldrich

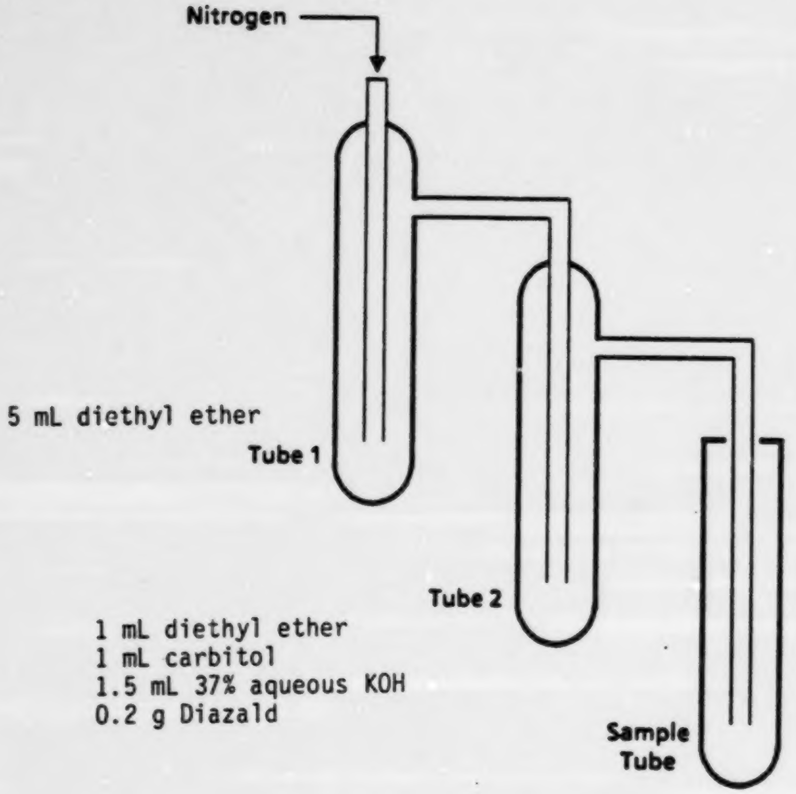

Nitrogen
5 mL diethyl ether
Tube 1
Tube 2
1 mL diethyl ether
1 mL carbitol
1.5 mL 37% aqueous KOH
0.2 g Diazald
Sample Tube

FIGURE 4.1. DIAZOMETHANE GENERATOR.

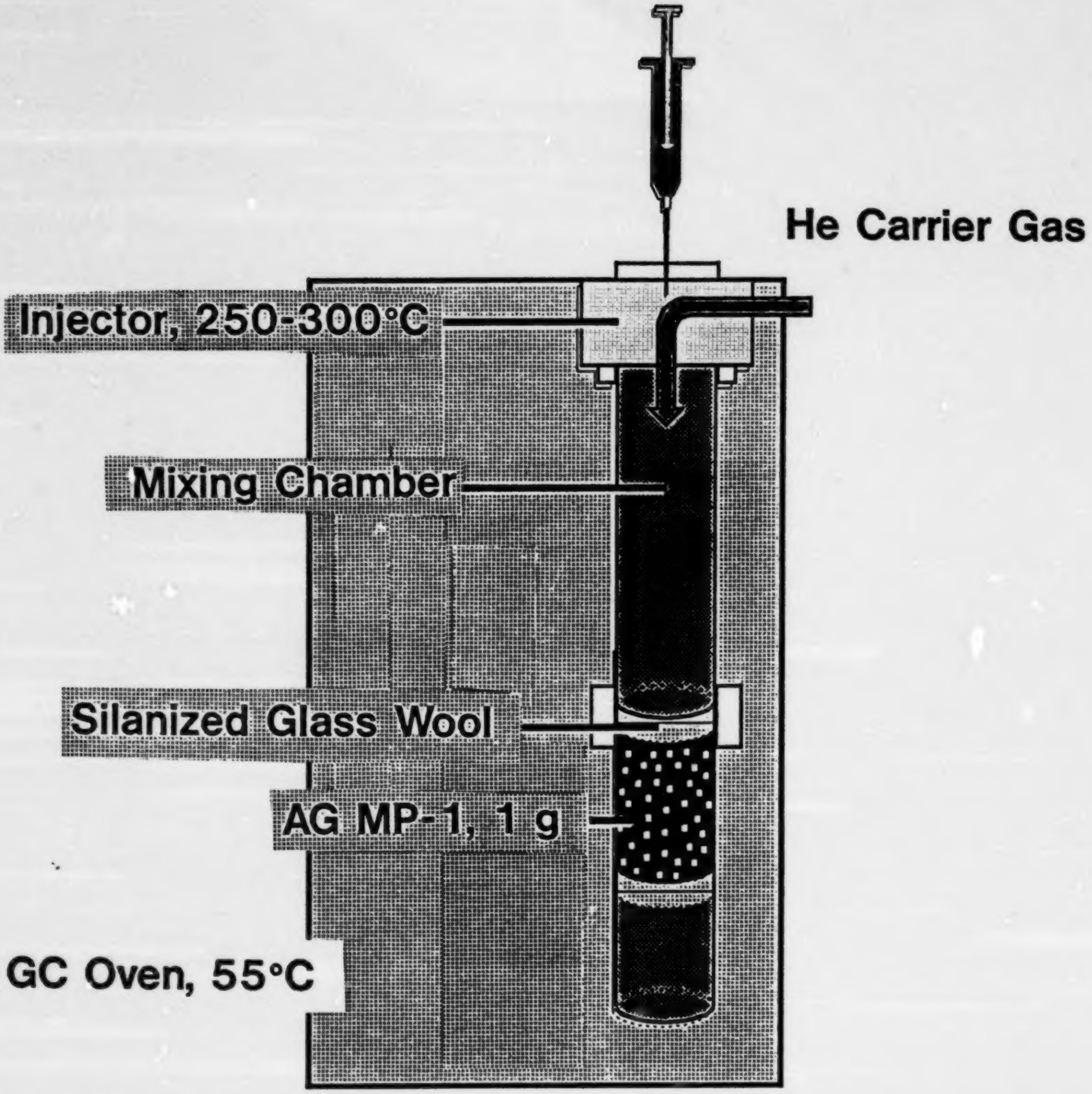

He Carrier Gas
Injector, 250-300°C
Mixing Chamber
Silanized Glass Wool
AG MP-1, 1 g
GC Oven, 55°C

FIGURE 4.2. SCHEMATIC REPRESENTATION OF VAPOR SPIKE METHOD

SECTION 5
RESULTS AND DISCUSSIONS

5.1 GC and GC/MS Analyses of Reference Standards

5.1.1 GC/FID Analysis of Phenols: GC/FID chromatograms showing chromatographic elution order, peak shape and general sensitivity for the laboratory evaluation phenols at 100, 10, 1, and 0.6 ng/μL levels are presented in Figures 5.1 and 5.2. Pentachlorophenol was not detected at levels ≲30 ng/μL. In general, peak shape and linearity were very good for all analytes. One column was used for GC/FID analyses during the 9 month program and chromatographic peak tailing was not significant during this time.

5.1.2 GC/ECD Analysis of Phenols: GC/ECD chromatograms showing chromatographic elution order, peak shape and general sensitivity for the five methylated laboratory evaluation phenols detectable by ECD are presented in Figures 5.3 and 5.4. Analyte levels in those standards were 0.2, 0.1, 0.05 and 0.00 ng/μL. The 0.00 ng/μL level was prepared as a methylation blank; one minor peak in this chromatogram co-eluted with pentachlorophenol and corresponded to a 0.005 ng/μl concentration level. Good peak shape, linearity and sensitivity were observed for the methylated phenol analytes, especially pentachlorophenol.

5.1.3 GC/FID Analysis of Neutral Interference Compounds: A GC/FID chromatogram showing elution order, peak shape and general sensitivity for the 7 neutral interference compounds is presented in Figure 5.5. Analytes in the standard mixture shown were present at either 100 or 10 ng/μL. All analytes were detected at the lowest concentration levels required for quantification of sorbent extracts, 1 or 0.1 ng/μL.

5.1.4 EI GC/MS Analysis of Phenols: A total ion current chromatogram from the EI GC/MS analysis of 29 phenolic/carboxylic acid analytes, 6 deuterated recovery standards and 1 internal standard is shown in Figure 5.6. The phenolic analytes were present in that mixture at 10 ng/μL. Because all analytes (except pentachlorophenol and hexanoic acid) were detected in the analysis of the lowest level standard (0.5 ng/μL) with S/N $\geq$3 for the base peak, quantification of analytes at this level in field samples was feasible.

5.1.5 NCI GC/MS Analysis of Phenols: A total ion current chromatogram from the NCI GC/MS analysis of the 14 laboratory evaluation phenols at 3 ng/μl is shown in Figure 5.7. The same 5 analytes which were detected by GC/ECD were also detected with good sensitivity by NCI GC/MS. The primary difference between the GC/ECD and NCI GC/MS analyses was the absence of methylation for the NCI GC/MS analysis. Despite the lack of methylation, pentachlorophenol was detected with good sensitivity and peak shape.

5.2 Extraction of Phenols from Acidic Methanol:MTBE

The following experiments were carried out to evaluate methods used to extract phenolic analytes from the acidic sorbent eluate into a neutral solvent. The neutral solvent MTBE was used, rather than methylene chloride, for compatibility with both FID and ECD analysis methods. Recovery of the phenolic analytes through this extraction procedure was determined so that extraction from the sorbent could be determined as a separate issue.

In Table 5.1 the recoveries of the phenols are compared on the basis of spike level and extraction method. Using the extraction method outlined in Section 4.4.1 (Method 1), the recoveries did not appear to be significantly different for the three analyte levels evaluated, except for 4-OH-indole and 2- and 3-NO_2-phenol. Because interferences to these analytes were not detected in the blank, it appeared that the GC injector and/or column was deactivated incrementally by each succeeding analysis. Because standard analyses were interspersed with samples, recoveries greater than 100% could occur. For these reasons, and for detection of pentachlorophenol at the lower spike levels, methylation and GC/ECD analyses were instituted in succeeding experiments.

Table 5.1 includes the recoveries of the phenols when using the extraction procedure detailed in Section 4.4.2 (Method 2). In general, there were no major differences between the values obtained for the two methods. For the sake of minor improvements, though, the latter extraction method (Section 4.4.2) was used in succeeding experiments. For these extraction methods, the variation observed in each set of replicate experiments was good, generally <5%.

The extraction efficiencies for these two methods were lower by approximately 5-10% relative to the method employed in the first study, carried out during the interval 6/88-9/88 at Battelle. Recoveries may have been higher in the earlier study because lower boiling methylene chloride was used as solvent instead of MTBE. Methylene chloride could not be used in any part of this study because of the GC/ECD analyses. Since the previous method required concentration from 150 mL to 1 mL and these methods required concentration from 15 mL to 1 mL, the disadvantage of slightly lower recovery here was offset by the advantage of a less cumbersome extraction procedure which provided equivalent, and low, variability among replicates and compatibility with GC/ECD analyses.

5.3 Extraction of Phenols from AG MP-1

5.3.1 Solvent Spike to Solvent-Slurried 20-50 mesh AG MP-1: The following experiments were carried out to assess collection efficiency of AG MP-1 for the phenols without the variables which might be introduced by vapor spiking. These experiments were also used to assess the extraction efficiency of acidic methanol:MTBE in removing all analytes from AG MP-1. In Table 5.2, the recoveries of the phenols from 20-50 mesh AG MP-1 are compared on the basis of spike level and extraction method. Using the first extraction method, detailed in Section 4.4.1, minor differences were observed in recoveries at the three spike levels. However, no trends were apparent; for some analytes, the lowest spike level showed highest recovery and for other analytes, the highest spike level showed highest recovery. Variability among replicates was small, generally $\leq$5%. Except for the highest spike level, the quantity of the spike which was not retained by the sorbent was negligible. Flow rate rather than sorbent capacity may have been responsible for the apparent breakthrough of phenolic analytes at the high spike level. The repeat of this experiment at the high spike level (using the second extraction method) showed no breakthrough of phenols.

The recovery values determined from GC/FID and GC/ECD analyses for 2-NO_2- and 6-CH_3-2-NO_2-phenol showed very good agreement. For samples spiked with 1 and 10 µg phenol quantities, the quantification of 3-NO_2-phenol from GC/FID data was discounted for reasons discussed in Section 5.2. Good agreement, then, between recovery values obtained from the two GC analysis methods for 2-NO_2- and 6-CH_3-2-NO_2-phenol provided a measure of assurance for the chlorinated phenol recoveries determined solely from GC/ECD data.

GC/FID and GC/ECD method blanks are shown in Figure 5.8. As seen there, a few minor peaks other than internal standards were observed. In the GC/FID analysis, a minor peak corresponding to phenol was detected, at a concentration <0.1 ng/µL. In the GC/ECD analysis of the blank, the components which were detected were also present in the methylation blank of standards and, thus, were not attributed to the sorbent or the extraction procedure.

The data in Table 5.2 confirmed the data in Table 5.1, that recoveries of phenols were not significantly different for the two slight variations in method used to extract the phenols from the acidic eluate into neutral solvent. However, recoveries of the phenols from 20-50 mesh AG MP-1 were, on the average, 8% lower than recoveries of phenols from the acidified methanol:MTBE (comparison of data for high spike level, second extraction method). These results indicated that extraction of the phenols from AG MP-1 was not complete and might be improved by increased contact time between sorbent and extraction solvent.

5.3.2 Solvent Spike to Dry 200-400 mesh AG MP-1: Phenols spiked to dry AG MP-1 were removed by several methods in one experiment set, as described in detail in Section 4.5.2. Since replicates of each extraction procedure were not performed, only major differences between the methods were determined. Recovery of phenols by each extraction procedure is given in Table 5.3.

Spiked sorbents 1 and 2 were eluted first with acidic eluant pumped through the sorbent tube. After transferring the sorbent to a vortex tube, the sorbent was extracted a second time. Differences in the distribution of phenols between the first and second acidic extracts of each spiked sorbent was used to assess efficiency of the extraction methods. As seen in Table 5.3, 2-NO_2-phenol was recovered to a much greater extent in the second acidic eluate of both spiked samples. No explanation for the behavior of this one compound could be discerned; however, that result indicated that solvent pumped through a sorbent tube might not be an effective method for other untested phenols.

Recoveries of phenols in the first extract of sorbent tubes 1 and 2 were compared to determine whether phenols whose non-polar end remained in a solvent film on the sorbent surface were extracted more efficiently than those whose non-polar end may have been adsorbed by the styrene-divinylbenzene sorbent backbone. Conclusions about the magnitude of such an effect were made by comparing total recoveries of spikes 1 and 2. As seen in Table 5.3, phenol recoveries in spiked sorbent 2 were lower than spiked sample 1 by 2-11% for 9 of the 12 compounds. These differences, though not large considering the fact that these were single analyses, tended to indicate that the sorbent backbone may have contributed to retention of phenols even after release of the phenolic end from the exchange site.

The third spiked sorbent was subjected to a He purge and then transferred directly to a vortex tube for a single extraction. Comparison of the recoveries of spiked sorbents 2 and 3 was used to assess the efficiency of the two extraction methods. Though recoveries in spiked sorbent 3 were lower than spiked sample 2 by 1-13% for 9 of the 12 compounds, the differences were not so large to offset the disturbing elution pattern for 2-NO_2-phenol noted previously. Because dual extraction of a sorbent would be too time-consuming, a single extraction with vortex action seemed most appropriate. The appearance of voids and air pockets in the sorbent tubes (for extractions performed with the HPLC pump) were also disturbing. Because these bubbles could not be removed completely, continued contact of sorbent and eluant could not be assured, and incomplete extraction would result.

5.3.3 Combined Extraction of Phenols from AG MP-1 and Acidic Eluate: Extraction of phenols from the sorbent directly to a neutral solvent appeared reasonable, as shown by the high phenol recoveries in Table 5.4. This extraction method was evaluated at the completion of this program, and thus was not used for any other samples generated on this program. Recovery of those analytes quantified by GC/FID, except 2-OH-biphenyl, was high, ≥ 78%. Data for 2,4-dichlorophenol and pentachlorophenol were not available because the extracts were not split for GC/ECD analyses. However, based on data for the remaining analytes, 2,4-diCl-phenol and Cl-phenol recoveries should be similar, and recovery of less polar pentachlorophenol should be similar to 2-OH-biphenyl.

The simplicity of this extraction method suggested that this method should be considered for future studies. Some modification of the procedure may be necessary to assure extraction of the less polar/more organic species such as 2-OH-biphenyl. This method should be beneficial for experiments involving larger sorbent quantities (e.g. sorbent quantities necessary for sampling at 1-4 L/min), because solvent volumes would not have to be increased significantly. The major change required would be an increase in the concentration of the aqueous HCl solution to provide adequate amounts of counterion (Cl-) for the increased number of exchange sites.

5.4 Extraction of Neutral Interference Compounds from AG MP-1

5.4.1 Extraction after Solvent Spike to Solvent-Slurried AG MP-1: Recoveries of neutral compounds in neutral solvents after spiking to a column of MTBE above 1 g of AG MP-1, both 20-50 and 200-400 mesh, were high, 83-102%. Recoveries of the high (10/1 mg), medium (1/0.1 mg) and low (0.1/0.01 mg) quantities spiked to the 20-50 mesh AG MP-1 sorbent are shown in Table 5.5. Recoveries of the high, medium, and low quantities spiked to the 200-400 mesh AG MP-1 sorbent are shown in Table 5.6. Because the first MTBE eluate was, in fact, the MTBE to which the neutral interference analytes were spiked initially, presence of these neutral analytes in that eluate indicated the extent to which they were not retained by the sorbent. More than 50% of each compound was not retained by the sorbent under these spiking conditions. The elution profile of each analyte, percent eluted in each succeeding fraction, was similar for the two sorbent mesh sizes evaluated. These results indicated that methods evaluated for one sorbent mesh may be reasonably applied to another mesh size without significant difference in results.

5.4.2 Extraction after Solvent Spike to Dry 200-400 mesh AG MP-1: Neutral compounds were eluted from AG MP-1 using methods described in Section 4.6.2. Because replicates of each elution were not performed, only major differences between the methods were determined. Total recovery of each neutral compound by each elution method is listed in Table 5.7. As seen there, these analytes were recovered quantitatively when the sorbent was not purged with He gas for removal of solvent. The lower recoveries for spiked sorbent 2, relative to spiked sorbent 1, probably indicated the extent to which analytes were purged from the sorbent when the spiking solvent was removed; with exception of very high boiling fluorenone (boiling point of 342 °C), recovery (or more accurately, recovery of the amount of analyte remaining) was proportional to boiling point. Recoveries of these analytes in spiked sorbent 3 appeared significantly lower. Substantial quantities of dodecane, tetradecane, biphenyl and fluorenone were detected in the acidic extract of spiked sorbent 3, possibly indicating the need for a longer extraction time for neutral compounds than was used here. The concerns arising from extractions with the low pressure pump, voids formed in sorbent beds and low recovery of 2-NO_2-phenol, were still the compelling reasons to choose vortex extraction of neutral and phenolic analytes in field-collected samples, despite the lower recovery from vortex-extracted spiked sorbent 3 of Table 5.7.

Phenolic analytes were not detected in any solvent used for extraction of the neutral compounds and phenol recoveries were high in the acidic eluates of the sorbent which followed these neutral eluates. These results indicated that when phenols were spiked as a solution to dry sorbent, the OH groups reacted quickly with exchange sites. These results indicated that deuterated phenols spiked prior to field sampling would be retained by chemical reaction with the exchange site, rather than adsorption to the polymer backbone.

A second evaluation of extraction procedures for the neutral compounds was completed during extraction of the Delaware field samples. For this reason, the results of this experiment were not incorporated into the extraction method of all field samples. As seen in Table 5.8, neutral compounds spiked to dry 200-400 mesh AG MP-1 were extracted using either sonication or vortex action. Similar extraction efficiencies were achieved when spiked sorbent was sonicated or vortexed in the 6 dram vials; recoveries averaged 92% in both cases. Sonication of the sorbent, though, produced many fines which were not readily separated from the solvent with centrifugation. Vortex extraction in the larger 50 mL centrifuge tubes resulted in an average recovery of 95%, presumably because of better mixing action.

5.5 Collection of Vapor Phase Phenols with Simulated Sampling

5.5.1 Comparisons of Sampling Rate and Dilution Chamber on Collection of Phenols with 20-50 mesh AG MP-1: Recoveries of laboratory evaluation phenols from 20-50 mesh AG MP-1 following simulated sampling at 10 and 20 mL/min sampling rates are shown in Table 5.9. As seen in the entire table, variability in recoveries (% rsd) for each experiment, performed in triplicate, was small, generally ≤ 10%. Because of relatively low variability within an experiment, differences in recoveries between experiments were considered significant, and were presumed to be due to these experimental conditions and not the subsequent extraction and analysis procedures.

Significantly lower recoveries were observed at the higher sampling rate of 20 mL/min, independent of the material used for the dilution and mixing chamber and independent of the average sorbent weight. In addition, though chamber wall losses were expected, phenol recoveries with the nickel chamber at the 10 mL/min sampling rate were unexpectedly higher than sampling without a chamber at 10 mL/min. As listed in Table 5.9, the average weight of sorbent for these two experiments was different, with slightly greater mass used for sampling at 10 mL/min with the nickel chamber. These observations together indicated 1) that phenols passed through the sorbent without having opportunity to react with sorbent active sites and 2) that breakthrough was dependent on sorbent mass.

The recoveries of phenols in Table 5.9 were normalized by average sorbent mass (listed in last row of Table 5.9) to produce the normalized recovery data recorded in Table 5.10. As seen there, normalized recoveries were similar for 100 μg of the low boiling point phenols sampled at 10 mL/min through sorbent alone and sorbent with the nickel dilution chamber. (Differences in recoveries of the higher boiling species, pentachlorophenol, 3-NO_2-phenol, 2-OH-biphenyl and 4-OH-indole, are discussed later in this section.) Normalized recoveries for 100 µg of the low boiling point phenols sampled at either 10 mL/min or 20 mL/min through the sorbent with the Teflon dilution chamber were slightly lower than those normalized recoveries obtained with the nickel chamber; differences were more pronounced at the higher sampling rate.

Although the data listed in Table 5.10 for the three experiments with the nickel dilution chamber suggested a non-ideal adsorption isotherm for collection of phenols with AG MP-1 (and, therefore, poor collection efficiency for truly dilute gas streams), later experiments demonstrated that this was, in fact, not the case. Because changes in sorbent mesh or superficial linear sampling velocity cannot compensate for non-ideal behavior, the variation in collection efficiency found in later experiments when these parameters were varied indicated that the trends observed in Table 5.10 must be due solely to kinetic effects. The extent of sorbent drying and consequent bead size differences, together with packing differences, may have been the parameters responsible for the results recorded in Table 5.10.

The ratios of normalized recoveries, as shown in Table 5.11, were used to assess the magnitude of adsorption caused by the differing dilution chamber materials. The ratio of normalized recovery (Teflon vs. nickel dilution chamber) for the phenols averaged 0.96 and 0.83 for the 10 and 20 mL/min sampling rates, respectively. These average relative recoveries indicated that approximately 4% and 17% of the spiked phenols were adsorbed by the Teflon, relative to nickel, at the 10 and 20 mL/min sampling rates. Because recoveries at 20 mL/min may be quite variable due to breakthrough losses alone, the most accurate estimate of loss to a Teflon surface was inferred from the data acquired with the 10 mL/min sampling rate. An average ratio of 1.00 for normalized recovery of phenols sampled without chamber vs. with nickel chamber indicated that adsorption to the nickel was negligible under these conditions. On the basis of these results, the nickel dilution chamber was used for subsequent experiments.

As shown in Table 5.12, amount of spike material recovered from the syringe at the completion of spiking was quite small, ~ 0.75% of the spike quantity. Each dilution chamber also contained relatively little material, < 0.5% of the spike quantity for the more volatile species. The relatively high boiling species were the only species detected in significant amounts in the dilution chambers. The mass balance for these four species is shown in Table 5.13. As seen there, total recovery for pentachlorophenol and 4-OH-indole was high, 94-100%. However, for 2-OH-biphenyl and 3-NO_2-phenol, material recovered in syringe and chamber did not account for all spiked material beyond that amount extracted from the sorbent. For these two analytes, and the remaining, lower boiling, species, we concluded that the unrecovered material in these experiments passed through the sorbent completely.

5.5.2 Comparisons of AG MP-1 mesh size on Collection of Phenols at 20 mL/min Sampling Rate: Collection efficiency of AG MP-1 was highly dependent upon the sorbent mesh size. In Table 5.14, results are listed for experiments in which 4 different mesh sizes were used to collect the vapor phase phenols at 20 mL/min sampling rate. As seen there, recoveries increased with increasing AG MP-1 mesh size (decreasing particle diameter). Highest recoveries were obtained with the 200-400 mesh AG MP-1. In general, the recoveries here with the 200-400 mesh AG MP-1 were similar to recoveries of phenols from AG MP-1 after solvent spike to solvent-slurried AG MP-1 (see Table 5.2) and only slightly lower than analytical method recoveries (recovery from acidified methanol:MTBE; see Table 5.1).

5.5.3 Comparisons of AG MP-1 mesh size on Collection of Phenols at 100 mL/min Sampling Rate: Since recoveries in the previous experiments were similar for 100-200 and 200-400 mesh AG MP-1, both mesh sizes were evaluated for collection efficiency at 100 mL/min. The 5 fold increase in sampling rate over previous experiments produced a dramatic difference in collection efficiency for the two mesh sizes. Though physically easier to manipulate and extract, the 100-200 mesh AG MP-1 did not collect vapor phase phenols efficiently at 100 mL/min; recoveries were generally 25-45%. In contrast, with the 200-400 mesh AG MP-1, recoveries were high (generally 75-85%) for the experiment in which 1 μg phenol quantities were spiked. The primary exception to this high recovery was pentachlorophenol; 22% on the sorbent and 21% remaining in the dilution chamber. The pentachlorophenol data here suggested that phenolic compounds containing bulky substituent groups adjacent to the OH could not interact efficiently with the sorbent at the superficial linear velocity being used (4.3 cm/sec). Reduction in superficial linear velocity could be achieved using a larger sorbent bed cross-section.

For two of the three experiments covered in Table 5.15 (10 μg spike to 100-200 mesh and 1 μg spike to 200-400 mesh), AG MP-1 was dried extensively before spiking (see Section 4.7.1). The slightly lower recoveries observed for the experiment in which 10 μg was spiked to 200-400 mesh AG MP-1 were probably due to channeling of phenols though the sorbent; prior to spiking, the sorbent may have dried and contracted after contact with the carrier gas of the injector system. On the basis of these results, extensive drying of the sorbent was deemed necessary.

5.5.4 Comparison of Superficial Linear Velocity on Collection of Phenols with 200-400 mesh AG MP-1: For experiments in which superficial linear velocity was reduced to 1.75 cm/sec, recovery of all phenols improved (relative to recovery with the 4.3 cm/sec superficial linear velocity), and recovery of pentachlorophenol improved dramatically. Because no dilution chamber was used in this experiment set, we expected complete transfer of analyte from the injector system to front end of sorbent. This transfer appeared to have occurred, and recoveries here were equivalent to or better than those for the extraction step evaluated initially (see Table 5.1). In Table 5.17, recoveries are compared for 1 μg of phenols collected at 100 mL/min sampling rate with superficial linear velocities of 4.3 and 1.75 cm/sec.

5.6 Stability of Sorbent-Bound Phenols

5.6.1 Stability During One Month Storage: The quantities of phenol and 3-CH_3-phenol recovered from AG MP-1 after storage on the sorbent for 1 month are shown in Table 5.18. As seen there, in comparison with other experimental data, recovery of phenol was slightly higher than recoveries of phenol in experiments wherein phenol was spiked to the sorbent and extracted immediately; recovery of 3-CH_3-phenol was intermediate between recoveries of 2-CH_3-phenol in those same experiments.

(Note: 3-CH_3-phenol, rather than 2-CH_3-phenol, was chosen for these experiments because it is the most reactive of the methyl-phenols, especially toward gas phase nitration.) A small quantity of phenol and 3-CH_3-phenol, amounts equal to 1% and 0.4%, respectively, of the spike level were found on the control sorbent tubes. Slight intrusion of ambient air through the end caps may have been responsible for these blank levels, however, this effect was minor. Due to the small number of samples and analytes analyzed in this study, definitive trends were not apparent. However, these preliminary results indicated that storage did not significantly affect recovery of these analytes.

5.6.2 Stability Toward HNO_3: The quantities of phenol and 3-CH_3-phenol recovered from AG MP-1 after 8 hr exposure to a 100 mL/min sample stream containing 6 ppbv HNO_3 are included in Table 5.18. As seen there, relative to recovery in other experiments, recovery of these analytes was not affected by the exposure. For both sorbent tube sizes, analyte recoveries were within the range of recoveries established by the baseline extraction efficiency experiments. When the recoveries of the exposed sorbent tubes were compared only to each other, though, the recoveries indicated that there may be some effect. In particular, lower phenol recoveries at the lower linear sampling velocity indicated that some reaction may have been possible with the increased contact time afforded by the lower velocity. This result, though, may be due solely to variation in data, because the GC/ECD analyses of these samples showed no detectable levels of those mono-nitration products which would be expected from ortho and/or para nitration. No other artifact species were detected. With the GC/ECD analysis method used, as little as 0.25% conversion of the parent phenol could have been detected. Therefore, nitration which might have occurred was quite limited.

5.7 Analyses of Field-Collected Samples

5.7.1 Recovery of Deuterated Spike Compounds from Delaware (Pigeon Point and Rifle Range; PP and RR) Collected Samples: The 9 Delaware field samples selected for analysis are listed in Table 5.19, together with the recoveries of the spiked deuterated phenols. As seen there, recoveries of the compounds spiked prior to sampling and prior to lab extraction were quite variable. However, the variation appeared to be due to several factors clearly demonstrated in these data. Concentration of sample extracts from 800 µL to 80 µL appeared to cause 30-60% loss of these analytes. These losses for the field recovery standards were deduced from recovery values measured at high and low volumes (800 and 80 µL, respectively) of the first sorbent extract for samples "PP 100 mL/min 8/4/89" and "RR 100 mL/min 8/7/89". In these samples, average losses due to the added concentration step were 55, 45, and 34% for phenol-d_6, 4-NO_2-phenol-d_4, and 2,4-diCl-phenol-d_3, respectively. Losses of 42, 39, and 63% for lab recovery standards 4-CH_3-phenol-d_5, 2-NO_2-phenol-d_4, and 2-Cl-phenol-d_4, respectively, were deduced from the data for the first extraction of the sorbent sample "PP 100 mL/min 8/4/89". Deuterated compound spike levels and the additional concentration step (from 800 µL down to 80 µL) were chosen on the assumption that analytes of interest might be present at levels slightly less than the target concentration level of 1 ppbv. The additional concentration was performed in hopes of detecting such species. Based on these and previous results, we concluded that concentrating by K-D evaporation to 1 mL did not result in significant losses of these semi-volatile compounds. However, a gentle stream of dry nitrogen could not be used to reliably concentrate these species below 1 mL.

The second factor which appeared to affect recovery of deuterated compounds was the sampling itself. The data suggest that during sampling or subsequent storage of sorbent tubes, the non-polar end of the phenols was adsorbed by the styrene-divinylbenzene polymer backbone of the sorbent. Though the addition of acidified methanol:MTBE rapidly released the phenolic end from the exchange site, extraction of the non-polar end may not have occurred as rapidly and may have resulted in retention of the phenols. For sorbent samples which were extracted a second time ("PP 100 mL/min 8/3/89", "PP Sector Blank 8/3/89", and "PP 100 mL/min 8/4/89"), significant quantities of the field recovery standards were found in the second extracts. MTBE or a mixture of methanol and MTBE may have been as efficient as acidified methanol:MTBE for recovering analytes in the second extraction, however, these neutral solvents were not tested. Since these second extracts were analyzed at only the higher volume of 800 µL, detection of additional quantities of the lab recovery standards was not possible. Additional quantities of these analytes were probably minimal, though, because these analytes were spiked just prior to extraction and did not undergo long storage times. In addition, recoveries of the lab recovery standards were generally about 50% and thus losses due to evaporative concentration of the extracts would fully account for the observed recoveries.

5.7.2 Recovery of Deuterated Compounds from Columbus Collected Field Samples: The additional samples collected in the Columbus area were analyzed solely for recovery of the spiked deuterated compounds. Several extraction and analysis methods were modified on the basis of previous results (Section 5.7.1) in hopes of achieving high recoveries for the deuterated spike compounds. Modifications are reviewed here, as follows. The quantity of the lab recovery compounds added to the sorbent was increased from 0.4 µg to 5 µg so that quantification could be accomplished at the 1 mL volume (200 µL was not removed for GC/ECD analysis). The sorbent samples were extracted twice with acidified methanol:MTBE, and both extracts were combined for a single analysis. The sorbent samples were also extracted in the 50 mL centrifuge tubes because these tubes appeared to provide better mixing of sorbent and eluant for extraction.

Recoveries of the field and lab recovery compounds, listed in Table 5.20, indicated that the modifications produced significantly higher recoveries, 60-120% for analytes other than 4-NO_2-phenol-d_4. Because 4-NO_2-phenol-d_4 was the most polar of the recovery analytes used, and the most difficult to quantify accurately, the recoveries for 4-NO_2-phenol-d_4 were different from recoveries of other deuterated compounds for several reasons. These analyses were performed using the currently available GC conditions of a second GC/MS instrument. Differences included a DB-5 column, splitless injection at 250 °C and helium carrier gas. The chromatographic conditions used in initial analyses, including a DB-1701 column, cool on-column injection and methane carrier gas, provided more favorable conditions for detection and quantification of 4-NO_2-phenol. For these reasons, recoveries of 4-NO_2-phenol-d_4 in these samples were generally discounted.

The higher recoveries of deuterated compounds in the field samples relative to the lab blank suggest that an internal standard more similar to the analytes of interest (e.g another deuterated phenol), rather than naphthalene-d_8, might provide more consistent results for samples. This suggestion is made because quantification of phenolic and acidic compounds may be affected by column activity more than a neutral PAH.

5.7.3 GC/ECD Analyses of Delaware Field Collected Samples: The chromatograms from the GC/ECD analyses of the 9 samples discussed in Section 5.7.2 are shown in Figures 5.9-5.17. The deuterated recovery standards (and internal standard) which were detected by GC/ECD are identified in these figures with the code used in Figure 5.9. Because a 15 m, rather than 30 m, DB-1701 column was used for these analyses, a chromatogram of the standard analytes is included (Figure 5.18) for visual display of retention times for these analyses. As seen in these chromatograms, very few major peaks were observed other than the deuterated recovery compounds, the internal standard and the methylation blank interferant (RT=10.5 min). Exceptions included the peak with RT=2.8 in PP samples and the peak with RT=8.45 (front shoulder of the methylated-2,4-diCl-phenol-d_3 peak) in one PP and one RR sample. Numerous minor components were observed and these components may be detected and identified in future studies if extracts are analyzed using NCI GC/MS (as discussed in Section 5.1.5). The similarity of GC/ECD chromatograms for the "PP Sector Blank 8/3/89" sample extract to the "PP 100 mL/min 8/3/89" sample extract, in regard to the component with RT=2.8, indicated that AG MP-1 was very efficient as a passive sampling sorbent.

5.7.4 Identification and Quantification of Phenols in Delaware Field Samples: The total ion current chromatograms from the EI GC/MS analyses of the PP and RR sample extracts are shown in Figures 5.19-5.27. The deuterated recovery compounds and internal standard for quantification are labelled in all figures as designated in the legend of Figure 5.19. For the sample PP 100 mL/min 8/3/89 (Figure 5.21), additional components are designated by compound class (e.g. aliphatic carboxylic acid) or mass of molecular ion (e.g. m/z 122 for a tentatively identified 3- and/or 4-OH-benzaldehyde).

As seen in these chromatograms, relatively few phenolic analytes were detected in the field samples collected at the Pigeon Point (PP) and Rifle Range (RR) sampling locations. The ambient phenolic pollutants detected in these samples included phenol (MW 94), a compound tentatively identified as a OH-CH_3-benzenemethanol (OH-CH_3-benzylalcohol) isomer (MW 138), and a compound tentatively identified as 3- and/or 4-OH-benzaldehyde (MW 122). Additional compounds identified by molecular ion (m/z 105, scan 350; m/z 136, scan 1020) were detected in the laboratory sorbent blank. Phenol was identified on the basis of spectrum and retention of authentic material in the calibration standards. The 3/4-OH-benzaldehyde isomer was identified by comparison with reference spectra in the NBS/EPA Mass Spectral Data Base; this compound was quantified using the relative response of 2-OH-benzaldehyde. The mass spectrum of the tentatively identified OH-CH_3-benzenemethanol isomer (Figure 5.45) was not found in any mass spectral data base; however, the proposed structure was consistent with mass spectral fragmentation patterns of similar compounds. This compound was quantified in samples using the relative response of 2-CH_3-phenol.

The recovery of phenol-d_6 in each sample was used to correct concentrations of native phenol and OH-CH_3-benzenemethanol for extraction/concentration losses. Since integrated areas of 3/4-OH-benzaldehyde in samples analyzed at "hi" and "low" solvent volumes (see Table 5.19, footnote c) indicated that losses of this analyte due to concentration of the extract were negligible, extract concentration levels of this analyte were not corrected. The resulting amount of phenol in each field sorbent extract was also corrected by the amount found in the laboratory sorbent blank (124 ng); the other two ambient phenol analytes were not detected in the laboratory sorbent blank. The net µg of each analyte in each field sample is listed in Table 5.21 together with the calculated ambient concentration. Among the PP samples acquired with dynamic sampling, the 8/3/89 20 mL/min PP sample was the only one showing ambient phenol levels greater than field blank levels. The higher ambient concentration observed for the lower sampling rate and the appearance of the sorbent when returned for analysis suggested that at the higher sampling rate additional drying and shrinkage of the sorbent occurred, with subsequent channeling of the air stream through the sorbent. The relatively high quantities of phenol in field and sector samples suggested that the sorbent was highly efficient at removing this analyte under passive diffusion conditions and that AG MP-1 would be an efficient sorbent for a passive sampler of proper design. Calculated ambient concentrations of the OH-CH_3-benzenemethanol isomer also suggested channeling of the air stream; ambient levels were higher when based upon the lower sampling rate data. These data for OH-CH_3-benzenemethanol did show, though, an increase (x 2.7) in quantity collected with the higher sampling rate. The filter preceding the 8/4/89 sorbent sample may have retained much of this compound; the sorbent-collected quantity in that sample was lower by a factor of 6 relative to the sample collected without a filter and significantly lower than any PP sample, including the sector sample. Despite relatively high field blank levels for 3/4-OH-benzaldehyde, the quantities collected on the sorbents, with exception of the sector sample, were significantly higher than the field blank. Again, channeling of the air stream was suggested by the higher quantities collected and higher ambient concentrations calculated for the sample collected at 20 mL/min relative to the one collected at 100 mL/min.

The samples collected at the RR site were more difficult to interpret. Again, relatively high field blank levels for phenol and 3/4-OH-benzaldehyde were observed and suggested diffusion of these analytes through the end caps. These surprisingly high levels also suggested that additional laboratory method blanks needed to be analyzed by GC/MS for quantification of 3/4-OH-benzaldehyde; this compound may be a background constituent of the sorbent that is extracted to a variable extent during the cleaning and activation of differing batches of sorbent. With exception of OH-CH_3-benzenemethanol, the analytes showed significantly high levels in the sector samples, indicative of efficient passive sampling.

5.7.5 Analysis of Field Samples Collected in Columbus: The total ion current chromatograms from EI and NCI GC/MS analyses of the sample collected in the Battelle parking lot are shown in Figure 5.28. Several compounds and compound classes are indicated in the chromatograms using the nomenclature given in Figure 5.21. The phthalate esters which were detected are likely laboratory contaminants, since neutral compounds were extracted from the sorbent prior to extraction of the phenols. The predominant compounds detected in the EI analysis were aliphatic carboxylic acids; the most abundant one was palmitic acid (hexadecanoic acid, $C_{16}H_{32}O_2$). As shown in Figure 5.29, diagnostic fragment ions for the aliphatic carboxylic acid compound class, m/z 60 and 73, can be plotted together with the total ion current chromatogram and used as a rapid screening tool for detection of a specific class in a relatively complex mixture.

In the NCI analysis, the NO_2-phenols were detected and several components were tentatively identified as OH-NO_2-indole isomers. One additional component, whose NCI mass spectrum is shown in Figure 5.30, was tentatively identified as a OH-diNO_2-cinnoline isomer ($C_8H_4N_4O_5$, MW 236). This is the first reporting of a mass spectrum consistent with OH-diNO_2-substitution from analysis of an environmental sample. Given the greater carcinogenic activity of azaarenes relative to the analogous PAH (e.g. quinoline is carcinogenic while naphthalene is not; see ref 3), the greater mutagenic activity of diNO_2-PAH relative to NO_2-PAH (e.g. mutagenicities toward TA 98, -S9 for 1-NO_2-pyrene and 1,6-diNO_2-pyrene are 1000 rev/μg and 160,000 rev/μg, respectively; see ref 4), and the greater bioavailability of OH-NO_2-PAH relative to NO_2-PAH (e.g. 3-, 6-, and 8-OH-1-NO_2-pyrene are the first mammalian metabolites formed from exposure to 1-NO_2-pyrene; see ref 5), the detection of this tentatively identified OH-diNO_2-cinnoline underscores the value of using NCI GC/MS analyses for detection of low level, biologically active compounds. The relative abundances of the components indicated by the NCI GC/MS chromatogram may not reflect the actual ambient relative abundances; concentration of the extract to 20 μL prior to analysis may have resulted in selective evaporation of the lower molecular weight and/or more volatile species.

The total ion current chromatograms from EI GC/MS analysis of the bus garage, composting facility, and laboratory method blank samples are shown in Figures 5.31, 5.32 and 5.33, respectively. The deuterated recovery standards and internal standard for quantification are identified as listed in the legend of Figure 5.31. The relative retention order of analytes is different from that listed in Figure 5.19 because a different

GC phase was used for these analyses (Section 4.9.3). The chromatogram from the analysis of the bus garage sample is displayed with 10 fold magnification due to the presence of a single component (aliphatic hydrocarbon, scan 970) at very high level.

In Figure 5.34, the intensity-normalized chromatograms from analyses of the bus garage sample and the method blank are compared. As shown there qualitatively, the levels in the blank were much lower than in the field sample. For comparison, levels of the deuterated recovery standards were in the range of 5-20 μg total in the sample, indicating analyte levels in the blank sample of 1-20 μg. Since neutral compounds were not extracted from the sorbent prior to extraction of the phenols, many neutral compounds were seen in these analyses. In order to estimate the relative levels of aliphatic hydrocarbons and aliphatic carboxylic acids in the two field samples, the ion current chromatograms for representative fragment ions of the two compound classes are displayed for each sample (Figures 5.35 and 5.36). With the most abundant peak for each ion presented as full scale, the relative abundance of the compound classes were estimated from the percent intensity of each ion listed in the upper left hand corner of each ion chromatogram. For the bus garage, aliphatic hydrocarbons appeared 10 times more abundant than aliphatic carboxylic acids, as indicated by the ratio of 50/5.2 for m/z 57 to m/z 60. For the compost facility, the comparison may not be valid since much fewer aliphatic hydrocarbons and aliphatic carboxylic acids were present at much lower levels. However, relative intensities of the ion current chromatograms indicated that aliphatic hydrocarbons may be 25 times more abundant than aliphatic carboxylic acids. The relatively higher levels of aliphatic carboxylic acids than alkyl-phenols in the Battelle parking lot sample (Figure 5.28, top) indicated that phenols may be present in the bus garage and composting facility samples at levels less than those indicated for the aliphatic carboxylic acids.

TABLE 5.1. RECOVERY OF ANALYTES FROM ACIDIC METHANOL:MTBE; COMPARISON OF EXTRACTION METHOD AND SPIKE LEVEL

	% Recovery (% rsd)				
	Extraction Method 1				Extraction Method 2
Analyte / Spike Level:	1 µg(a)	10 µg(a)	100 µg(a)	Ave of All Levels	100 µg(a)
Phenol	87 (4)	84 (3)	85 (<1)	85	86 (3)
2-CH_3-phenol	86 (4)	86 (3)	86 (<1)	86	87 (3)
4-CH_3-phenol	93 (6)	87 (2)	86 (1)	89	88 (3)
2,3-diCH_3-phenol	86 (4)	87 (1)	87 (2)	87	89 (2)
2-Cl-phenol	87 (5)	84 (5)	86 (<1)	86	86 (3)
4-Cl-phenol	86 (4)	88 (2)	88 (2)	87	89 (2)
2,4-diCl-phenol	102 (13)	87 (5)	85 (2)	86(c)	87 (2)
PentaCl-phenol	ND(b)	ND	111 (3)	-	97 (4)
2-NO_2-phenol	116 (20)	91 (3)	85 (<1)	88(c)	87 (3)
3-NO_2-phenol	151 (31)	102 (11)	92 (2)	97(c)	95 (1)
6-CH_3-2-NO_2-phenol	91 (6)	86 (<1)	89 (2)	89	88 (2)
2-OH-benzaldehyde	89 (5)	89 (4)	81 (1)	86	85 (3)
2-OH-biphenyl	88 (2)	91 (4)	89 (2)	89	92 (2)
4-OH-indole	38 (10)	41 (76)	67 (4)	49	78 (17)

(a) n = 3

(b) Not detected.

(c) Average at 10 and 100 µg levels.

TABLE 5.2. RECOVERY OF ANALYTES FROM 20-50 MESH AG MP-1: COMPARISON OF EXTRACTION METHOD AND SPIKE LEVEL

	% Recovery (% rsd); % Remaining in Solvent(a)											
	Extraction Method 1									Extraction Method 2		
Analyte	Spike Level: 1 µg(b)			10 µg(b)			100 µg(b)			100 µg(b)		
Phenol	104	(1)	0	80	(7)	<.1	79	(5)	4	76	(8)	.2
2-CH$_3$-phenol	90	(<1)	0	84	(6)	<.1	82	(5)	5	80	(8)	.2
4-CH$_3$-phenol	89	(3)	1	81	(6)	.3	82	(4)	5	79	(8)	.3
2,3-diCH$_3$-phenol	88	(<1)	0	84	(5)	<.1	84	(3)	5	82	(7)	.3
2-Cl-phenol	83	(<1)	0	82	(6)	0	81	(5)	4	78	(6)	.1
4-Cl-phenol	81	(<1)	0	81	(5)	0	84	(2)	5	82	(6)	.2
2,4-diCl-phenol	ND			ND			86	(4)	0	84	(5)	0
ECD(c)	85	(2)	NA(d)	78	(6)	NA	NA			NA		
PentaCl-phenol	ND			ND			126	(4)	0	111	(8)	0
ECD	78	(3)	NA	79	(8)	NA	NA					
2-NO$_2$-phenol	76	(3)	0	77	(7)	0	84	(3)	1	81	(5)	<.1
ECD	72	(4)	NA	75	(6)	NA	NA			NA		
3-NO$_2$-phenol	152	(3)	0	94	(5)	<.1	90	(<1)	4	86	(4)	<.1
ECD	87	(10)	NA	67	(7)		NA			NA		
6-CH$_3$-2-NO$_2$-phenol	82	(<1)	0	82	(6)	0	84	(3)	4	82	(5)	<.1
ECD	82	(3)	NA	76	(6)	NA	NA			NA		
2-OH-benzaldehyde	76	(2)	0	70	(10)	0	78	(4)	2	78	(4)	<.1
2-OH-biphenyl	85	(2)	0	82	(5)	<1	84	(<1)	6	82	(5)	.3
4-OH-indole	ND			ND			13	(4)	7	32	(8)	.3

(a) % of spiked material which passed through sorbent bed without being adsorbed.

(b) n = 3

(c) Results from GC/ECD analysis of above named compound.

(d) Sample not analyzed by GC/ECD.

TABLE 5.3. RECOVERY OF PHENOLS FROM 200-400 MESH AG MP-1 WITH DIFFERING ELUTION METHODS AFTER SOLVENT SPIKE TO DRY SORBENT

	% Recovery by Elution Method						
	Spike 1(a) No GC He Purge Elution with Pump/Vortex(b)			Spike 2(a) GC He Purge Elution with Pump/Vortex			Spike 3(a) GC He Purge Vortex Tube Extraction
Analyte	Acid 1	Acid 2	Total	Acid 1	Acid 2	Total	Acid 1
Phenol	86	2	88	80	1	81	76
2-CH_3-phenol	75	2	76	71	0	71	70
4-CH_3-phenol	79	2	81	70	0	70	118
2,3-diCH_3-phenol	58	2	60	60	0	60	57
2-Cl-phenol	86	1	87	84	0	84	77
4-Cl-phenol	91	1	92	89	0	89	82
2,4-diCl-phenol	101	2	103	105	0	105	105
PentaCl-phenol(c)	ND	ND	ND	ND	ND	ND	ND
2-NO_2-phenol	11	72	83	9	68	77	82
3-NO_2-phenol	79	3	81	85	0	85	80
6-CH_3-2-NO_2-phenol	74	1	75	93	2	95	82
2-OH-benzaldehyde	89	1	90	90	0	90	85
2-OH-biphenyl	85	2	87	85	0	85	77

(a) n = 1; spike level = 100 μg.

(b) Acid 1 = % of phenol spike eluted with pump

Acid 2 = % of phenol spike eluted with second extraction using vortex action.

(c) Acquisition error prevented detection.

TABLE 5.4. RECOVERY OF PHENOLS FROM 200-400 MESH AG MP-1 WITH COMBINED EXTRACTION PROCEDURES AFTER SOLVENT SPIKE TO DRY SORBENT

Compound	% Recovery,	(% rsd)(a)
Phenol	101	(2)(b)
2-CH_3-phenol	82	(9)
4-CH_3-phenol	88	(3)
2,3-diCH_3-phenol	78	(7)
2-Cl-phenol	84	(7)
4-Cl-phenol	85	(7)
2,4-diCl-phenol	ND(c)	
PentaCl-phenol	ND	
2-NO_2-phenol	251(d)	(9)
3-NO_2-phenol	215(d)	(11)
6-CH_3-2-NO_2-phenol	119(d)	(8)
2-OH-benzaldehyde	120	(8)
2-OH-biphenyl	62	(11)

(a) n = 3; 1 µg spike level.

(b) n = 2 due to apparent contamination in spike 3; % deviation from the mean listed.

(c) Methylation and GC/ECD analysis not performed for detection and quantification of this analyte.

(d) Recovery from GC/FID data; more accurate quantification anticipated if methylation and GC/ECD used.

TABLE 5.5. RECOVERY OF NEUTRAL INTERFERENCE COMPOUNDS FROM 20-50 MESH AG MP-1 IN NEUTRAL SOLVENTS: SOLVENT SPIKE TO SLURRIED AG MP-1

Analyte level,mg	% Recovery in Sequential AG MP-1 Eluate MTBE(a) 1 10 mL(c)	MTBE 2 10 mL	MEOH(b) 1 10 mL	MEOH 2 10 mL	Total
Decane					
10 mg(d)	83	10	1	ND	94
1 mg(d)	70	15	ND	ND	85
0.1 mg(d)	75	20	ND	ND	95
					Ave = 91
Dodecane					
10 mg	83	10	1	ND	94
1 mg	70	15	ND	ND	85
0.1 mg	75	20	ND	ND	95
					Ave = 91
Tetradecane					
10 mg	85	10	2	ND	97
1 mg	70	15	ND	ND	85
0.1 mg	70	20	ND	ND	90
					Ave = 91
o-Xylene					
10 mg	83	10	1	ND	94
1 mg	70	15	ND	ND	85
0.1 mg	70	20	ND	ND	90
					Ave = 90
Naphthalene					
1 mg	75	15	1	ND	91
0.1 mg	75	20	ND	ND	95
0.01mg	70	25	ND	ND	95
					Ave = 94
Biphenyl					
1 mg	85	15	1	ND	101
0.1 mg	65	20	ND	ND	85
0.01mg	70	25	ND	ND	95
					Ave = 94
Fluorenone					
1 mg	70	15	6	1	92
0.1 mg	55	25	1	ND	81
0.01mg	50	25	ND	ND	75
					Ave = 83

(a) methyl-t-butyl-ether

(b) methanol

(c) elution volume used

(d) n = 3

TABLE 5.6. RECOVERY OF NEUTRAL INTERFERENCE COMPOUNDS FROM 200-400 MESH AG MP-1 IN NEUTRAL SOLVENTS: SOLVENT SPIKE TO SLURRIED AG MP-1

Analyte	% Recovery in Sequential AG MP-1 Eluate					
Level	MTBE 1 10 mL	MTBE 2 10 mL	MTBE 3 10 mL	MEOH 1 10 mL	MEOH 2 10 mL	Total
Decane						
10 mg(a)	75	9	<0.1	ND	ND	84
1 mg(a)	76	12	ND	ND	ND	88
0.1 mg(a)	77	15	ND	ND	ND	92
						Ave = 88
Dodecane						
10 mg	74	9	<0.1	ND	ND	83
1 mg	75	12	ND	ND	ND	87
0.1 mg	75	15	ND	ND	ND	90
						Ave = 87
Tetradecane						
10 mg	75	9	<0.1	ND	ND	84
1 mg	74	12	ND	ND	ND	86
0.1 mg	74	14	ND	ND	ND	88
						Ave = 86
o-Xylene						
10 mg	74	10	0.1	ND	ND	84
1 mg	75	13	0.1	ND	ND	88
0.1 mg	76	16	ND	ND	ND	92
						Ave = 88
Naphthalene						
1 mg	85	15	1	1	ND	102
0.1 mg	79	20	2	1	ND	102
0.01 mg	75	23	2	3	ND	103
						Ave = 102
Biphenyl						
1 mg	87	14	1	1	ND	102
0.1 mg	80	18	2	1	ND	101
0.01 mg	77	21	3	3	ND	104
						Ave = 102
Fluorenone						
1 mg	71	18	1	6	ND	97
0.1 mg	59	20	3	9	ND	91
0.01 mg	54	19	3	6	ND	82
						Ave = 90

(a) n = 3

TABLE 5.7. RECOVERY OF NEUTRAL INTERFERENCE COMPOUNDS FROM 200-400 MESH AG MP-1 WITH DIFFERING ELUTION METHODS AFTER SOLVENT SPIKE TO DRY SORBENT

	% Total Recovery for Analyte by Elution Method(a)		
Analyte	Spike 1(b) No GC He Purge Elution With Pump	Spike 2(b) GC He Purge Elution With Pump	Spike 3(b) GC He Purge Vortex Tube Extraction
Decane	95	1	1
Dodecane	95	47	27
Tetradecane	95	78	76
o-Xylene	94	2	2
Naphthalene	100	84	75
Biphenyl	100	89	75
Fluorenone	96	91	66

(a) High level of neutral interference compounds spiked; sum of recovered analytes in three sequential MTBE and two sequential MEOH solvent extraction volumes is listed.

This table presents companion data to Table 5.3 for the phenols. Both phenols and neutral interference compounds were spiked to the sorbent tubes.

(b) n = 1

TABLE 5.8. RECOVERY OF NEUTRAL INTERFERENCE COMPOUNDS FROM 200-400 MESH AG MP-1 WITH DIFFERING EXTRACTION METHODS AFTER SOLVENT SPIKE TO DRY SORBENT

	% Total Recovery for Analyte by Extraction Method[a]		
Analyte	Spike 1[b] Sonify in 6 Dram Vial	Spike 2[b] Vortex in 6 Dram Vial	Spike 3[b] Vortex in 50 mL Centrifuge Tube
Decane	88	89	95
Dodecane	94	94	96
Tetradecane	95	94	96
o-Xylene	85	88	93
Naphthalene	97	96	98
Biphenyl	96	95	97
Fluorenone	90	89	92

(a) Medium level interference compound spike; sum of recovered material in three sequential MTBE and 2 sequential MEOH solvent extraction volumes.

(b) n = 2

TABLE 5.9. RECOVERY OF PHENOLS FROM AG MP-1 AFTER VAPOR SPIKING: COMPARISON OF SAMPLING RATE AND DILUTION CHAMBER MATERIAL

(100 µg Spike; 20-50 Mesh; 7 mm I.D. Sorbent Tube)

	% Recovery with Designated Dilution Chamber, (% rsd)									
	Sorbent Only[a]		Nickel Chamber[b]				Teflon Chamber[c]			
Sampling rate\	10 mL/min		10 mL/min		20 mL/min		10 mL/min		20 mL/min	
Phenol	60	(6)	79	(5)	45	(11)	65	(10)	39	(6)
2-CH$_3$-phenol	61	(6)	82	(4)	45	(11)	66	(15)	38	(6)
4-CH$_3$-phenol	60	(4)	79	(4)	44	(11)	65	(13)	38	(7)
2,3-diCH$_3$-phenol	61	(11)	84	(4)	47	(10)	68	(17)	39	(8)
2-Cl-phenol	61	(4)	78	(5)	52	(6)	66	(3)	45	(5)
4-Cl-phenol	62	(4)	81	(5)	51	(7)	68	(8)	42	(6)
2,4-diCl-phenol	69	(3)	88	(5)	49	(5)	69	(10)	42	(7)
PentaCl-phenol	95	(12)	72	(7)	58[d]		74[e]	(17)	56	(1)
2-NO$_2$-phenol	67	(4)	83	(7)	49	(4)	66	(6)	42	(6)
3-NO$_2$-phenol	60	(27)	28	(3)	19	(27)	25	(40)	19	(30)
6-CH$_3$-2-NO$_2$-phenol	67	(3)	85	(5)	58	(4)	71	(3)	50	(5)
2-OH-benzaldehyde	68	(9)	95	(5)	55	(6)	68	(10)	48	(5)
2-OH-biphenyl	55	(10)	35	(9)	26	(20)	31	(20)	25	(31)
4-OH-indole	26	(121)	18	(38)	21	(47)	20	(56)	24	(24)
g AG MP-1	0.791	(14)	1.029	(0.6)	1.166	(1.6)	0.866	(16)	1.193	(4)

(a) 1 g of AG MP-1 in tube (7 mm id x 5 cm length) attached to exit of GC injector (configuration = GC injector - AG MP-1); inj temp = 250°C; inj. time = 40 sec; n = 3; post injection sweep volume = 300 mL.

(b) Configuration = GC injector - Nickel chamber (5 mm id x 10 cm length) - AG MP-1; inj. time = 60 sec; all other conditions same as (a); n = 3.

(c) Configuration = GC injector - Teflon chamber (5 mm id x 10 cm length) - AG MP-1; all other conditions see (b).

(d) n = 1

(e) n = 2

TABLE 5.10. NORMALIZED RECOVERY OF PHENOLS FROM 20-50 MESH AG MP-1 AFTER VAPOR SPIKING

Analyte	Normalized Recovery with Designated Dilution Chamber, %[a]					
	Sorbent	Nickel Chamber			Teflon Chamber	
sampling rate (mL/min)	10	10	20	20[b]	10	20
spike level (µg)	100	100	100	10	100	100
Phenol	76	77	39	25	75	33
2-CH_3-phenol	77	80	39	25	76	32
4-CH_3-phenol	76	77	38	27	75	32
2,3-diCH_3-phenol	77	82	40	27	79	33
2-Cl-phenol	77	76	45	28	76	38
4-Cl-phenol	78	79	43	29	79	35
2,4-diCl-phenol	87	86	42	39	80	35
PentaCl-phenol	120	70	50	30	85	47
2-NO_2-phenol	85	81	42	37	76	35
3-NO_2-phenol	76	27	16	27	29	16
6-CH_3-2-NO_2-phenol	85	83	50	37	82	42
2-OH-benzaldehyde	86	92	47	29	79	40
2-OH-biphenyl	70	34	22	28	36	21
4-OH-indole	33	17	18	ND	23	20

(a) Data from Table 5.9; normalized recovery calculated as average recovery/average resin bed weight; while this method is, in strictest terms, not the most accurate calculation of average normalized recovery, it will be fairly accurate since the sorbent quantities for each set of replicates were similar.

(b) Data not included in Table 5.9 or 5.11.

TABLE 5.11. RATIO OF ANALYTE RECOVERY ON 20-50 MESH AG MP-1 FOR VAPOR SPIKES (NORMALIZED FOR AG MP-1 QUANTITY)

	Ratio of Recovery					
Tef_{20}/Tef_{10}	Teflon/Ni[a]	Teflon/Ni		AG MP-1/Ni(b)	AG MP-1/Tef	Ni_{20}/Ni_{10}
Analyte	10 ml/min	20 ml/min	10 ml/min	10 ml/min		
Phenol	.99	.85	.99	1.01	.50	.44
2-CH_3-phenol	.96	.82	.98	1.01	.49	.41
4-CH_3-phenol	.97	.83	.99	1.01	.49	.42
2,3-diCH_3-phenol	.96	.79	.95	.98	.49	.41
2-Cl-phenol	1.01	.85	1.03	1.01	.59	.50
4-Cl-phenol	.99	.80	1.00	1.00	.56	.46
2,4-diCl-phenol	.94	.83	1.01	1.09	.49	.44
pentaCl-phenol(c)	1.22	.94	1.73	1.41	.71	.55
2-NO_2-phenol	.95	.84	1.05	1.11	.52	.46
3-NO_2-phenol(c)	1.07	.95	2.81	2.63	.61	.54
6-CH_3-2-NO_2-phenol	1.00	.85	1.03	1.03	.60	.52
2-OH-benzaldehyde	.86	.85	.92	1.09	.50	.50
2-OH-biphenyl(c)	1.05	.92	2.03	1.94	.66	.59
4-OH-indole(c)	1.32	1.13	1.90	1.42	1.01	.88
Average(d)	.96	.83	1.00	1.03	.52	.46

(a) $\frac{\text{recovery with Teflon chamber}}{\text{ave. wt resin bed (Tef)}} \div \frac{\text{recovery with Ni chamber}}{\text{ave. wt resin bed (Ni)}}$

(b) Normalized recovery with sorbent/normalized recovery with Ni chamber; see Tables 5.9 and 5.10.

(c) Analyte with greater percentage of recovered material in chamber rinse than in AG MP-1.

(d) Average of ratios except for analytes denoted by (c).

TABLE 5.12. RECOVERY OF ANALYTES IN SYRINGE RINSE AND DILUTION CHAMBER RINSE FOR VAPOR SPIKES AT 20 ML/MIN SAMPLING RATE WITH NICKEL OR TEFLON DILUTION CHAMBER

Analyte	% Recovery of Spike; (%rsd)[a]							
	Spike with Nickel Chamber				Spike with Teflon Chamber			
	Syringe		Nickel Chamber		Syringe		Teflon Chamber	
Phenol	0.74	(6)	0.01	(83)	0.72	(4)	0.02	
2-CH_3-phenol	0.77	(6)	0	(0)	0.75	(4)	0.03	
4-CH_3-phenol	0.73	(6)	0.05	(23)	0.72	(5)	0.15	(12)
2,3-diCH_3-phenol	0.79	(6)	0.07	(27)	0.78	(7)	0.25	(46)
2-Cl-phenol	0.68	(5)	0	(0)	0.67	(3)	<0.01	
4-Cl-phenol	0.68	(7)	0.24	(19)	0.68	(7)	0.60	(41)
2-4-diCl-phenol	ND		ND		ND		ND	
PentaCl-phenol	ND		42	(10)	ND		40	(13)
2-NO_2-phenol	0.77	(1)	0.47	(3)	0.79	(4)	0.51	(8)
3-NO_2-phenol	0.95	(<1)	41	(8)	0.97	(7)	35	(20)
6-CH_3-2-NO_2-phenol	0.59	(6)	0.01	(50)	0.58	(5)	0.06	
2-OH-benaldehyde	0.58	(4)	0.01	(18)	0.58	(3)	<0.01	
2-OH-biphenyl	0.77	(7)	39	(14)	0.78	(8)	29	(19)
4-OH-indole	2.51	(15)	71	(13)	1.66	(9)	68	(20)

(a) n = 3; see Table 5.9 for recovery of analytes from 20-50 Mesh AG MP-1; spike level = 100 µg/analyte.

TABLE 5.13. MASS BALANCE FOR ANALYTES DETECTED AT SIGNIFICANT LEVELS IN DILUTION CHAMBER WITH 20 ML/MIN SAMPLING RATE FOR VAPOR SPIKE

		Recovery, %							
		With Nickel Chamber				With Teflon Chamber			
Analyte	bp°C	Total	Resin	Syringe	Chamber	Total	Resin	Syringe	Chamber
2-OH-biphenyl	282	66	26	1	39	55	25	1	29
3-NO_2-phenol	272[b]	61	19	1	41	55	19	1	35
4-OH-indole	--	95	21	3	71	94	24	2	68
PentaCl-phenol	310	100	58	0	42	96	56	0	40

(a) n = 3; see Tables 5.9 and 5.12 for data; spike level = 100 μg/analyte.
(b) bp for 4-NO_2-phenol; bp for 3-NO_2-phenol is probably similar.

TABLE 5.14. NORMALIZED RECOVERY OF ANALYTES FROM AG MP-1 AFTER VAPOR SPIKING: COMPARISON OF RECOVERY WITH AG MP-1 MESH SIZE

(10 μg Spike; 7 mm I.D. Tube; 20 mL/min Sampling Rate; Nickel Dilution Chamber)

Analyte	Normalized Recovery, %[a]							
mesh size	20-50		50-100		100-200		200-400	
particle diameter (um)	1180-300		300-150		150-75		75-38	
sampling rate (mL/min)	20		20		20		20	
spike level (ug)	10		10		10		10	
Phenol	25		52		79		80	
2-CH_3-phenol	25		53		82		81	
4-CH_3-phenol	27		52		81		81	
2,3-diCH_3-phenol	27		54		83		81	
2-Cl-phenol	28		49		78		80	
4-Cl-phenol	29		51		82		84	
2,4-diCl-phenol	39		58		96		99	
PentaCl-phenol	30	(100)[b]	26	(58)	48	(71)	56	(75)
2-NO_2-phenol	37		53		76		81	
3-NO_2-phenol	27	(61)	36	(50)	81	(89)	88	(98)
6-CH_3-2-NO_2-phenol	37		52		85		87	
2-OH-benzaldehyde	29		59		91		92	
2-OH-biphenyl	28	(66)	50	(51)	80	(80)	81	(82)
4-OH-indole	ND	(94)	ND	(66)	ND	(39)	ND	(57)

(a) n=3; normalized recovery calculated as average recovery/average resin bed weight.

(b) sum of analyte quantities extracted from AG MP-1 and quantity rinsed from Nickel dilution chamber.

TABLE 5.15. RECOVERY OF PHENOLS AFTER VAPOR SPIKE: COMPARISON OF MESH SIZE AND ANALYTE SPIKE LEVEL

(100 mL/min Sampling Rate; 7 mm I.D. Sorbent Tube)

Analyte	% Recovery					
mesh size	100-200(a)		200-400(a)		200-400(b)	
sampling rate (mL/min)	100		100		100	
spike level (μg)	10		10		1	
Phenol	38		70		85	
2-CH_3-phenol	41		72		78	
4-CH_3-phenol	41		72		90	
2,3-diCH_3-phenol	45		73		82	
2-Cl-phenol	37		68		82	
4-Cl-phenol	37		73		77	
2,4-diCl-phenol	29		63		70	
PentaCl-phenol	8	(22)(c)	33	(39)	22	(43)
2-NO_2-phenol	16		83		61	
3-NO_2-phenol	22	(22)	38	(41)	39	(69)
6-CH_3-2-NO_2-phenol	24		71		68	
2-OH-benzaldehyde	39		83		82	
2-OH-biphenyl	39		71		77	

(a) n = 3

(b) n = 2

(c) Total recovered in sorbent and dilution chamber rinse.

TABLE 5.16. RECOVERY OF PHENOLS AFTER VAPOR SPIKE: 200-400 Mesh AG MP-1; 1 μg Phenol 100 mL/min Sampling Rate; 11 mm I.D. Sorbent Tube

Analyte	% Recovery	(% DM)(a)
Phenol	91	1
2-CH_3-phenol	87	1
4-CH_3-phenol	92	8
2,3-diCH_3-phenol	82	2
2-Cl-phenol	85	5
4-Cl-phenol	89	2
2,4-diCl-phenol	92	2
PentaCl-phenol	82	(b)
2-NO_2-phenol	82	(b)
3-NO_2-phenol	99	5
6-CH_3-2-NO_2-phenol	92	2
2-OH-benzaldehyde	101	7
2-OH-biphenyl	86	2

(a) n = 2; % deviation from the mean.

(b) Single analysis; analyte recoveries were 33% and 6% in 2nd sorbent extract for 2-NO_2-phenol and pentaCl-phenol, respectively.

TABLE 5.17. RECOVERY OF PHENOLS AFTER VAPOR SPIKE: COMPARISON OF LINEAR VELOCITY

(200-400 Mesh AG MP-1; 1 μg Phenol
100 mL/min Sampling Rate)

Analyte	% Recovery	
tube I.D.	7 mm	11 mm
linear velocity, (cm/sec)	4.3	1.75
Phenol	85	91
2-CH_3-phenol	78	87
4-CH_3-phenol	90	92
2,3-diCH_3-phenol	82	82
2-Cl-phenol	82	85
4-Cl-phenol	77	89
2,4-diCl-phenol	70	92
PentaCl-phenol	22 (43) (a)	82
2-NO_2-phenol	61	82
3-NO_2-phenol	39 (69)	99
6-CH_3-2-NO_2-phenol	68	92
2-OH-benzaldehyde	82	101
2-OH-biphenyl	77	86

(a) Total recovered in sorbent and dilution chamber rinse.

TABLE 5.18. RECOVERY OF PHENOL AND 3-CH_3-PHENOL FROM 200-400 MESH AG MP-1:COMPARISON OF STORAGE AND HNO_3 EXPOSURE STABILITY

	% Recovery	
Experiment	Phenol	3-CH_3-Phenol
Recovery from Acidic Methanol:MTBE	86	87[(a)]
Recovery from Solvent-Slurred AG MP-1	76	80[(a)]
Recovery from Dry AG MP-1	76	70[(a)]
Recovery after 1 month[(b)] room temp storage	80	74
Recovery after HNO_3 exposure[(c)] 4.3 cm/sec linear sampling velocity (7 mm I.D. tube)	85	86
Recovery after HNO_3 exposure[(c)] 1.75 cm/sec linear sampling velocity (11 mm I.D. tube)	76	77

(a) Recovery value for 2-CH_3-phenol; see Tables 5.1, 5.2 and 5.3.

(b) n = 2

(c) n = 1

TABLE 5.19. RECOVERY OF DEUTERATED COMPOUNDS FROM FIELD COLLECTED SAMPLES

Sample Designation				% Recovery					
				Field Recovery Std 20 μg(a)			Lab Recovery Std 0.4 μg(a)		
				Phenol-d_6	4-NO_2-phenol-d_4	2,4diCl phenol-d_3	4-CH_3-phenol-d_5	2-NO_2-phenol-d_4	2-Cl-phenol-d_4
PP Field Blank	8/3/89	extr 1(b)	lo vol(c)	20	25	22	30	25	21
PP 20 mL/min	8/3/89	extr 1	lo vol	48	53	73	37	63	77
PP 100 mL/min	8/3/89	extr 1	lo vol	38	40	76	30	50	79
		extr 2	hi vol	8	35	20	3	ND	ND
		total		46	75	96	33	50	79
PP Sector Blank	8/3/89	extr 1	lo vol	36	9	20	48	26	13
		extr 2	hi vol	26	32	58	3	ND	ND
		total		62	41	78	51	26	13
PP 100 mL/min	8/4/89	extr 1	hi vol	45	40	70	ND	ND	ND(d)
		extr 1	lo vol	19	18	53	50	61	37
		extr 2	hi vol	8	18(e)	18	ND	ND	ND
		total(f)		53	58	88	58	61	37(g)
RR 100 mL/min	8/6/89	extr 1	hi vol	40	40	70	ND	ND	ND
RR 100 mL/min	8/7/89	extr 1	hi vol	48	48	75	ND	ND	ND
		extr 1	lo vol	23	31	43	15	46	39
RR Field Blank	8/7/89	extr 1	lo vol	44	83	56	55	54	44
RR Sector Blank	8/7/89	extr 1	lo vol	42	3	9	45	ND	20
Lab Blank 1(h)		extr 1	lo vol	54	149	65	56	57	47
Lab Blank 2(h)		extr 1	lo vol	86	283	95	90	88	78

(a) Quantity spiked to AG MP-1 of each analyte.

(b) Designation of first or second extraction of AG MP-1 with acidic methanol:MTBE.

(c) Designation of volume at which sample analyzed; sample extracts initially concentrated to 1 mL; 200 μL removed for GC/ECD analysis; analysis of 1-2 μL of remaining 800 μL designated "hi vol"; for samples concentrated from 800 μL to 80 μL, analysis of 1-2 μL of 80 μL solution designated "lo vol".

(d) Lab recovery standards cannot be detected in "hi vol" sample extracts due to detection limits of GC/MS analysis method.

(e) Lower limit to that value; GC column began to degrade with consequent irreversible adsorption and tailing of 4-NO_2-phenol.

(f) Total recovery = sum of extr 1, hi vol, and extr 2, hi vol.

(g) Lab recovery standard added just prior to concentrating sorbent extract from 15 mL to 1 mL; analyte recoveries listed here reflect losses during concentration.

(h) Lab blanks spiked with 1.6 μg of field recovery standards; poor chromatography for 4-NO_2-phenol-d_4 at this level.

TABLE 5.20. RECOVERY OF DEUTERATED COMPOUNDS FROM COLUMBUS, OHIO COLLECTED SAMPLES

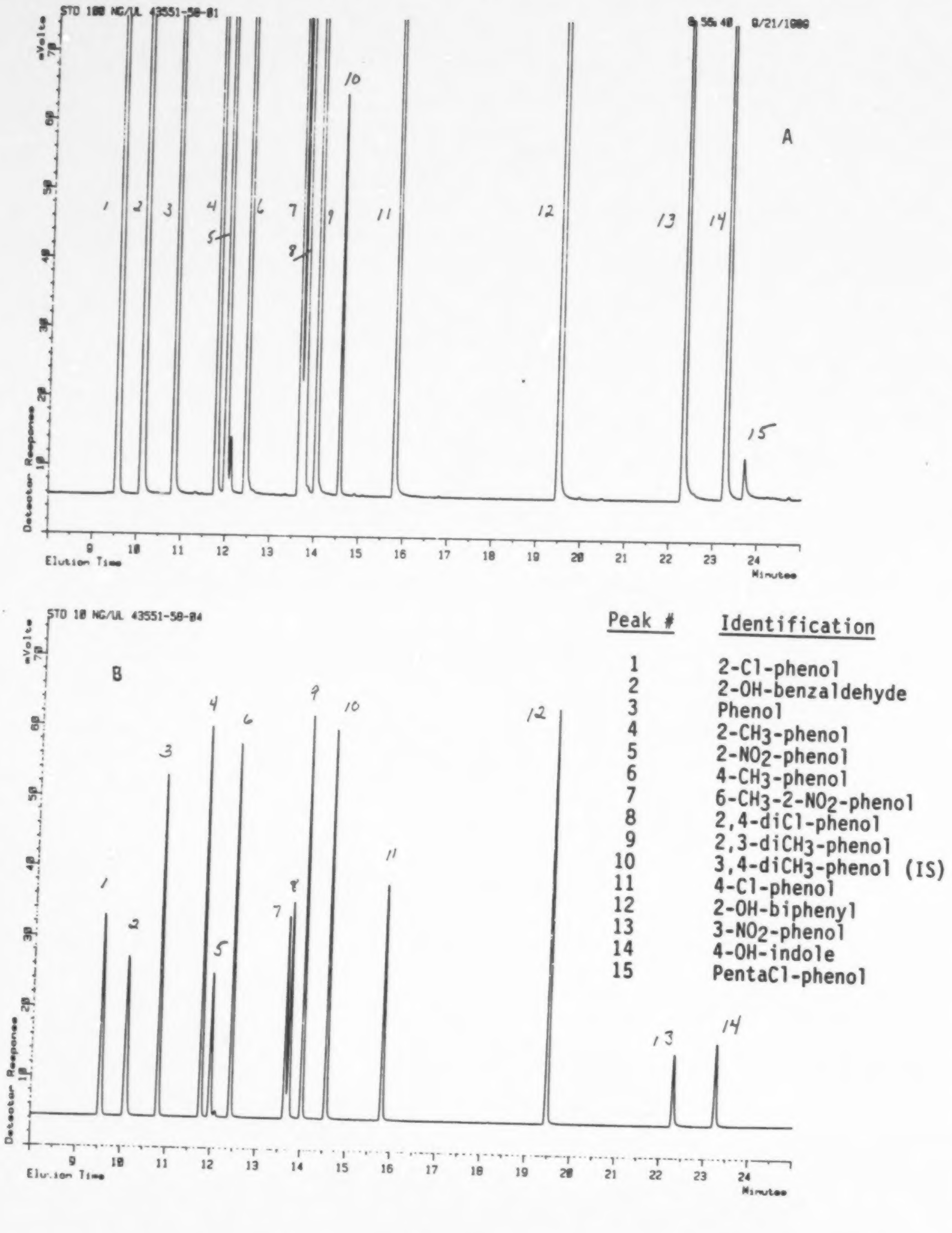
Sample Designation	% Recovery					
	Field Recovery Standard 20 µg			Lab Recovery Standard 5 µg		
	Phenol-d$_6$	4-NO$_2$-phenol-d$_4$	2,4-diCl-phenol-d$_3$	4-CH$_3$-phenol-d$_5$	2-NO$_2$-phenol-d$_4$	2-Cl-phenol-d$_4$
Municipal Bus Garage	103	80	100	108	120	106
Municipal Compost Facility	98	39	68	104	42	91
Lab Blank	69	47	89	90	66	62

TABLE 5.21 CONCENTRATIONS OF PHENOLIC ANALYTES FROM DELAWARE FIELD SAMPLES

Sample	net μg/sample [a] ($\mu g/m^3$) [b]		
	Phenol	OH-CH_3-benzenemethanol	3/4-OH-benzaldehyde
PP Field Blank 8/3	0.22 (1.7)	0 (0)	0.36 (2.8)
PP 20 mL/min 8/3	0.13 (5.1)	1.54 (60)	0.95 (38)
PP 100 mL/min 8/3	0.16 (1.3)	4.17 (33)	0.64 (5.0)
PP Sector 8/3	0.20 (1.5)	1.24 (9.8)	0.24 (1.9)
PP 100 mL/min 8/4	0.20 (1.5)	0.72 (5.2)	0.46 (3.3)
RR Field Blank 8/7	0.18 (1.3)	0.01 (<0.1)	3.06 (21)
RR 100 mL/min 8/7	0.005(<0.1)	0.11 (0.7)	0.36 (2.5)
RR Sector 8/7	0.28 (1.9)	1.17 (8.1)	0.09 (0.6)

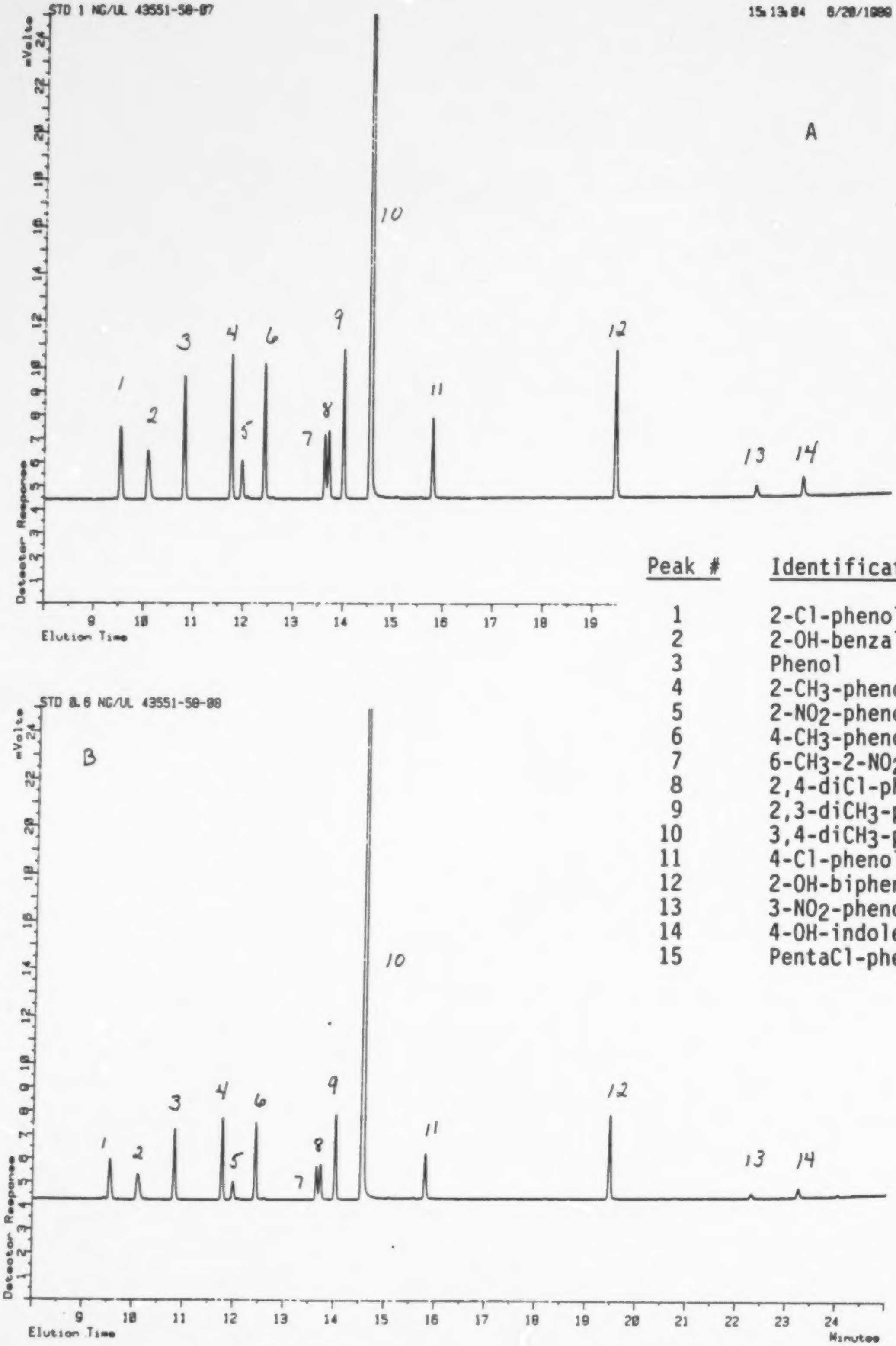
(a) net ng = (total ng/sample) - (total ng/sorbent method blank sample); sorbent method blank sample levels: phenol 124 ng; OH-CH_3-benzenemethanol, 0 ng; 3/4-OH-benzaldehyde, 0 ng.

(b) Field blanks and sector samples use sample volume of corresponding 100 mL/min sample.



Peak #	Identification
1	2-Cl-phenol
2	2-OH-benzaldehyde
3	Phenol
4	2-CH_3-phenol
5	2-NO_2-phenol
6	4-CH_3-phenol
7	6-CH_3-2-NO_2-phenol
8	2,4-diCl-phenol
9	2,3-diCH_3-phenol
10	3,4-diCH_3-phenol (IS)
11	4-Cl-phenol
12	2-OH-biphenyl
13	3-NO_2-phenol
14	4-OH-indole
15	PentaCl-phenol

FIGURE 5.1. CHROMATOGRAM FROM GC/FID ANALYSIS OF PHENOLS
A-100 ng/µL; B-10 ng/µL



Peak #	Identification
1	2-Cl-phenol
2	2-OH-benzaldehyde
3	Phenol
4	2-CH_3-phenol
5	2-NO_2-phenol
6	4-CH_3-phenol
7	6-CH_3-2-NO_2-phenol
8	2,4-diCl-phenol
9	2,3-diCH_3-phenol
10	3,4-diCH_3-phenol (IS)
11	4-Cl-phenol
12	2-OH-biphenyl
13	3-NO_2-phenol
14	4-OH-indole
15	PentaCl-phenol

FIGURE 5.2. CHROMATOGRAM FROM GC/FID ANALYSIS OF PHENOLS
A-1 ng/µL; B-0.6 ng/µL

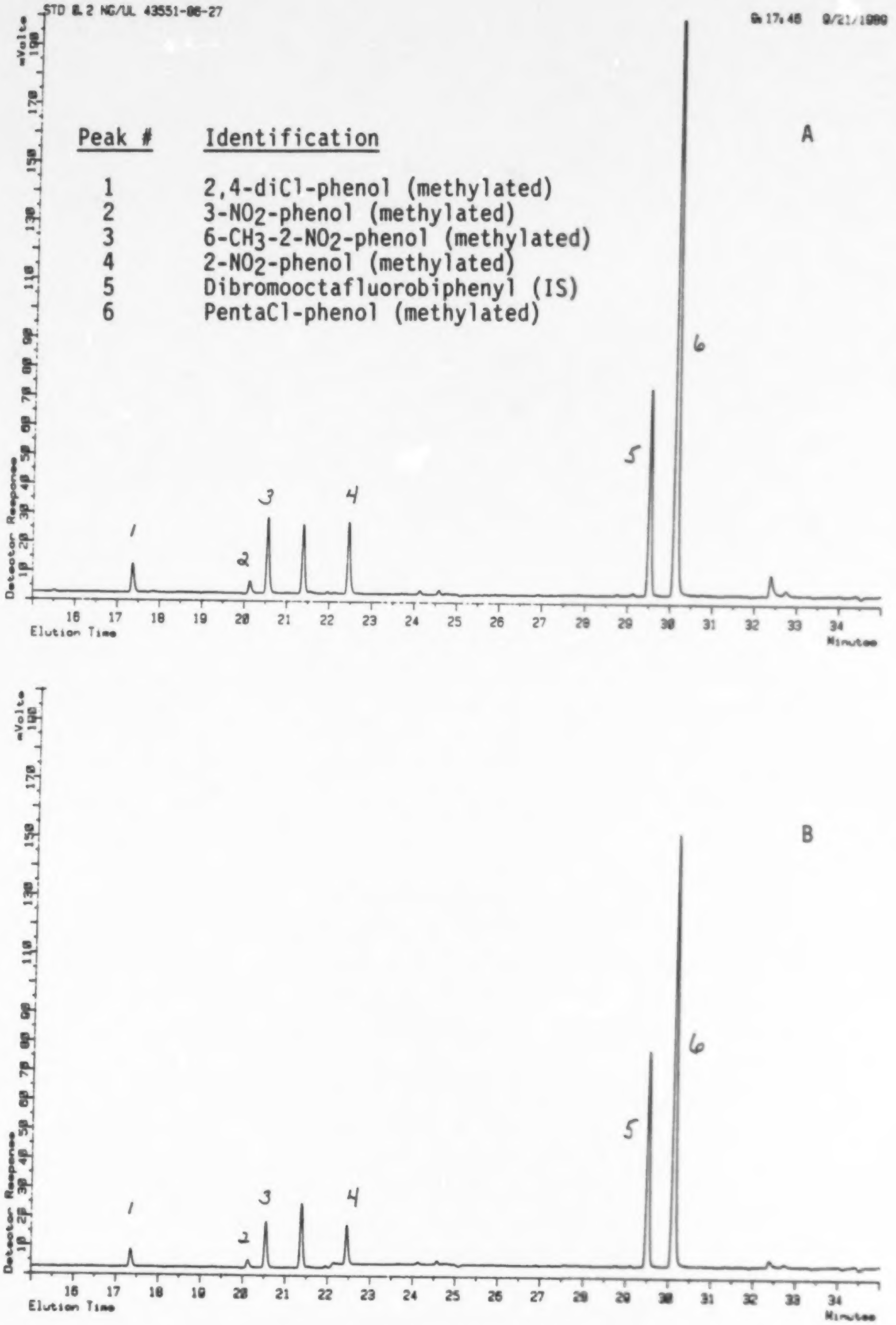
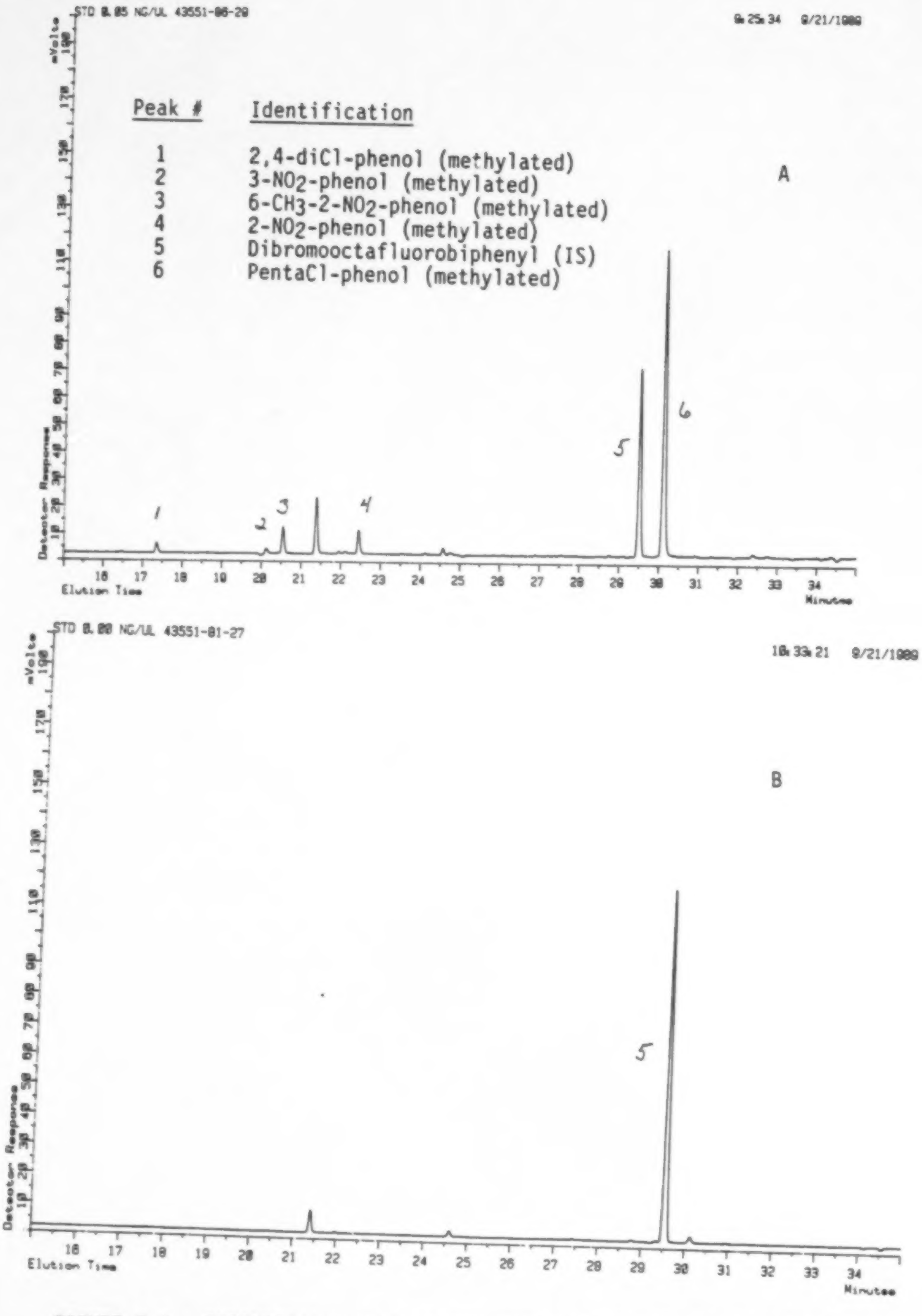


FIGURE 5.3. CHROMATOGRAM FROM GC/ECD ANALYSIS OF METHYLATED PHENOLS
A-0.2 ng/μL; B-0.1 ng/μL



Peak #	Identification
1	2,4-diCl-phenol (methylated)
2	3-NO_2-phenol (methylated)
3	6-CH_3-2-NO_2-phenol (methylated)
4	2-NO_2-phenol (methylated)
5	Dibromooctafluorobiphenyl (IS)
6	PentaCl-phenol (methylated)

FIGURE 5.4. CHROMATOGRAM FROM GC/ECD ANALYSIS OF METHYLATED PHENOLS A-0.05 ng/µL; B-METHYLATION BLANK

Peak #	Identification
1	o-Xylene
2	Decane
3	Dodecane
4	Naphthalene
5	Tetradecane
6	Biphenyl
7	Fluorenone

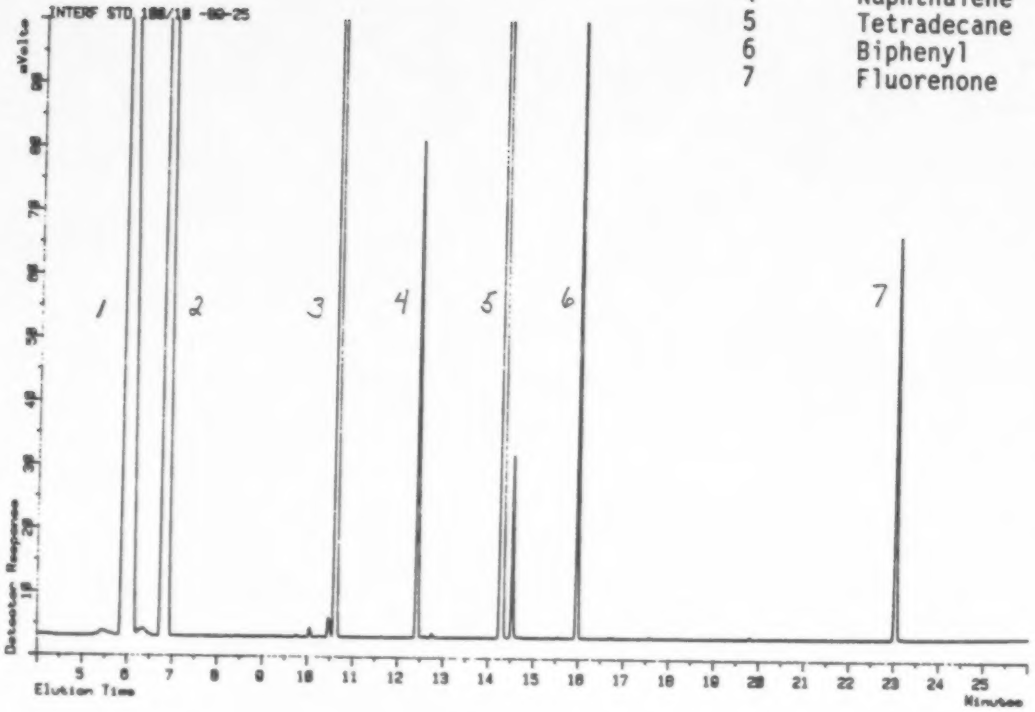


FIGURE 5.5. CHROMATOGRAM FROM GC/FID ANALYSIS OF NEUTRAL INTERFERENCES COMPOUNDS, 100/10 ng/μL (SEE TABLE 4.2)

Peak #	Identification
1	2-Cl-phenol; 2-Cl-phenol-d_4
2	2-OH-benzaldehyde; hexanoic acid
3	Phenol; phenol-d_6
4	2-NO_2-phenol; 2-NO_2-phenol-d_4
5	2-CH_3-phenol
6	2,6-diCH_3-phenol; naphthalene-d_8
7	4-CH_3-phenol; 4-CH_3-phenol-d_5
8	2,4-diCH_3-phenol; 2,5-diCH_3-phenol; 6-CH_3-2-NO_2-phenol
9	2,4-diCl-phenol; 2,4-diCl-phenol-d_3
10	2,6-diCl-phenol
11	4-CH3-2-NO_2-phenol
12	2,3-diCH_3-phenol
13	5-CH_3-2-NO_2-phenol
14	3,4-diCH_3-phenol
15	4-Cl-phenol
16	2,4,6-triCl-phenol
17	2-OH-biphenyl
18	Dodecanoic acid
19	2-CH_3-3-NO_2-phenol
20	3-NO_2-phenol
21	4-CH_3-3-NO_2-phenol
22	6-CH_3-3-NO_2-phenol
23	PentaCl-phenol
24	4-NO_2-phenol; 4-NO_2-phenol-d_4
25	3-CH_3-NO_2-phenol
26	2-CH_3-4-NO_2-phenol

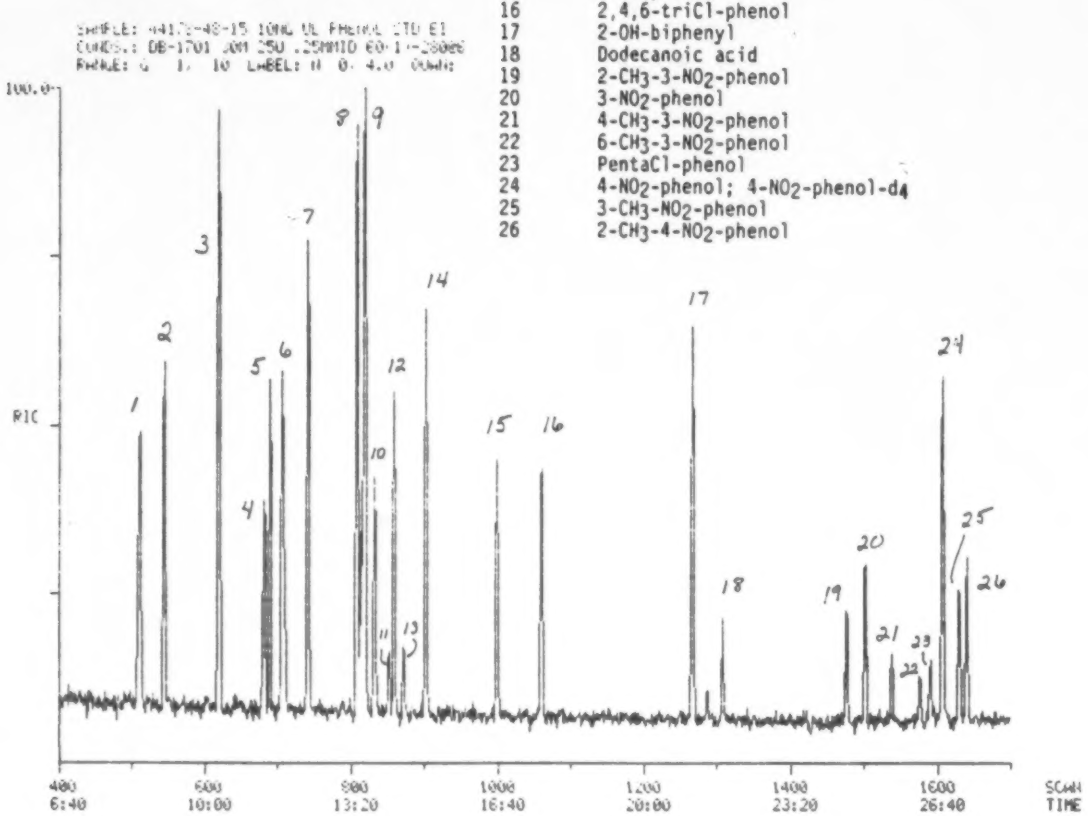


FIGURE 5.6. CHROMATOGRAM FROM EI GC/MS ANALYSIS OF PHENOLS AND ACIDS

Peak #	Identification
1	2-NO_2-phenol
2	6-CH_3-2-NO_2-phenol
3	2,4-diCl-phenol
4	3-NO_2-phenol
5	PentaCl-phenol

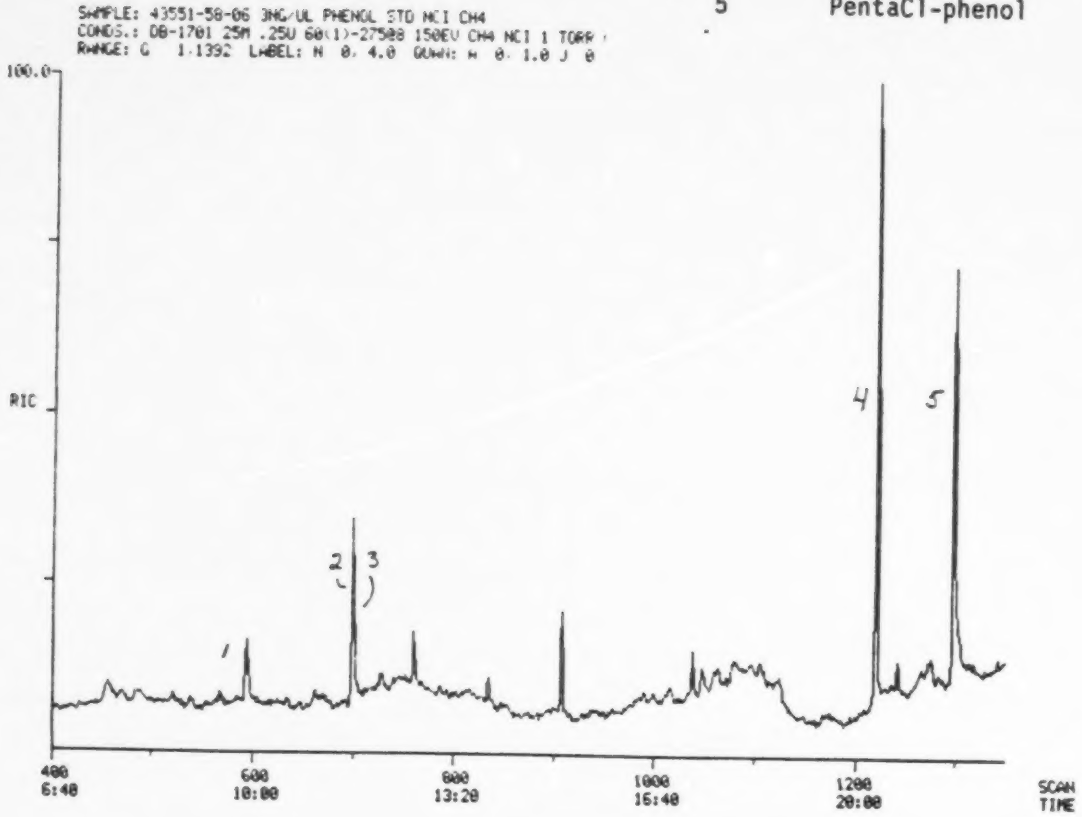
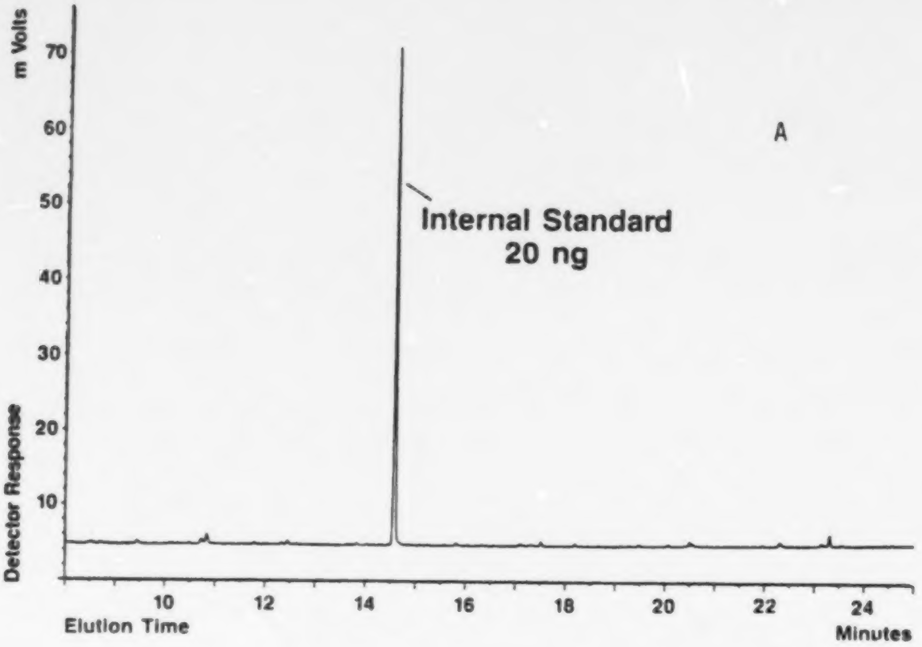


FIGURE 5.7. CHROMATOGRAM FROM NCI GC/MS ANALYSIS OF PHENOLS



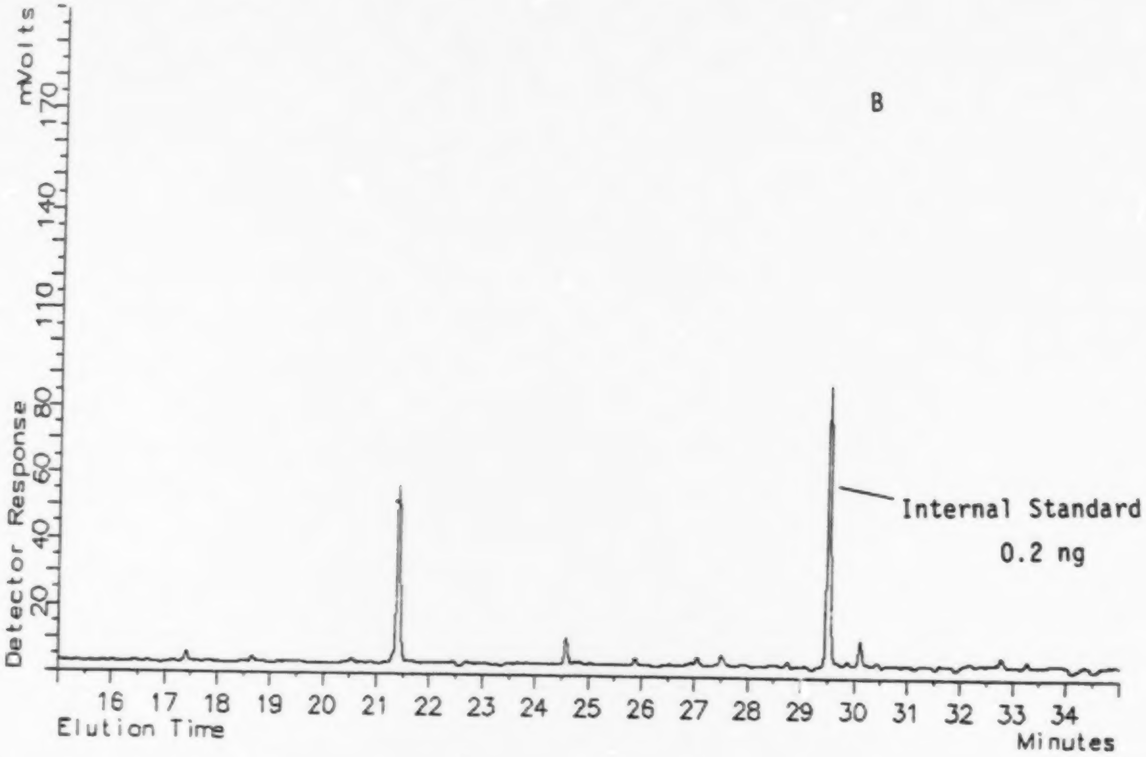


FIGURE 5.8. CHROMATOGRAMS FROM GC ANALYSES OF AG MP-1 EXTRACTION METHOD BLANK; A- GC/FID, B- GC/ECD

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

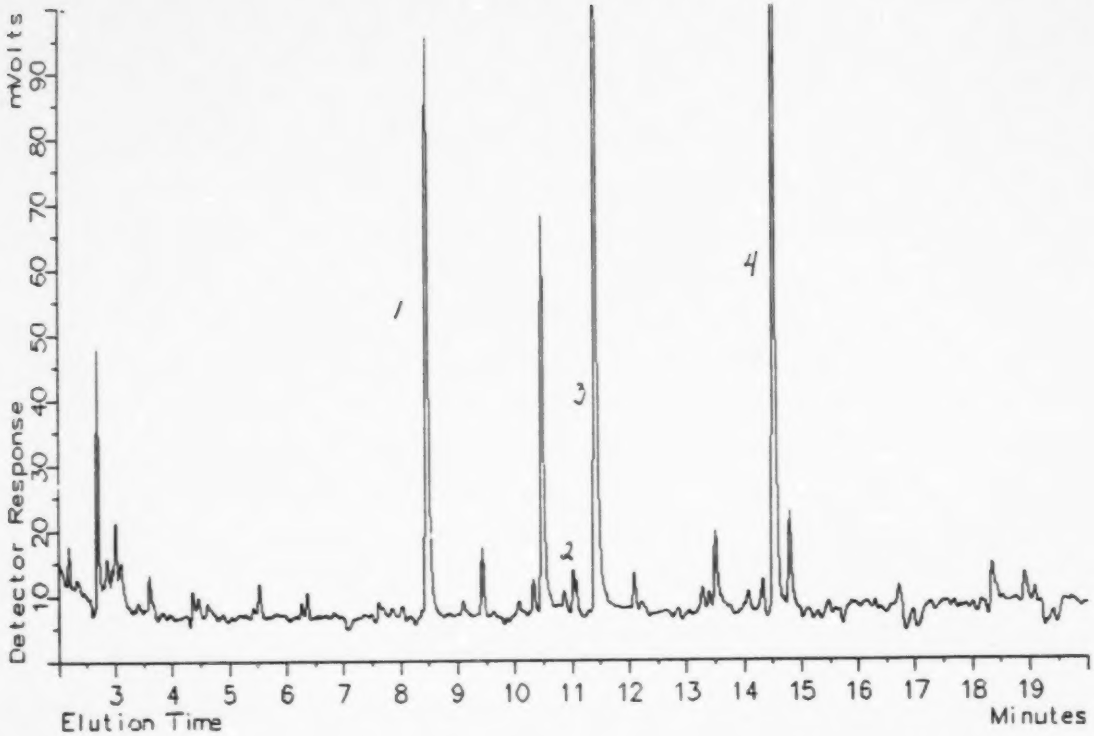


FIGURE 5.9. GC/ECD ANALYSIS OF PP FIELD BLANK 8/3/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d$_3$	methylated
2	2-NO$_2$-phenol-d$_4$	methylated
3	4-NO$_2$-phenol-d$_4$	methylated
4	DBOB (IS)	

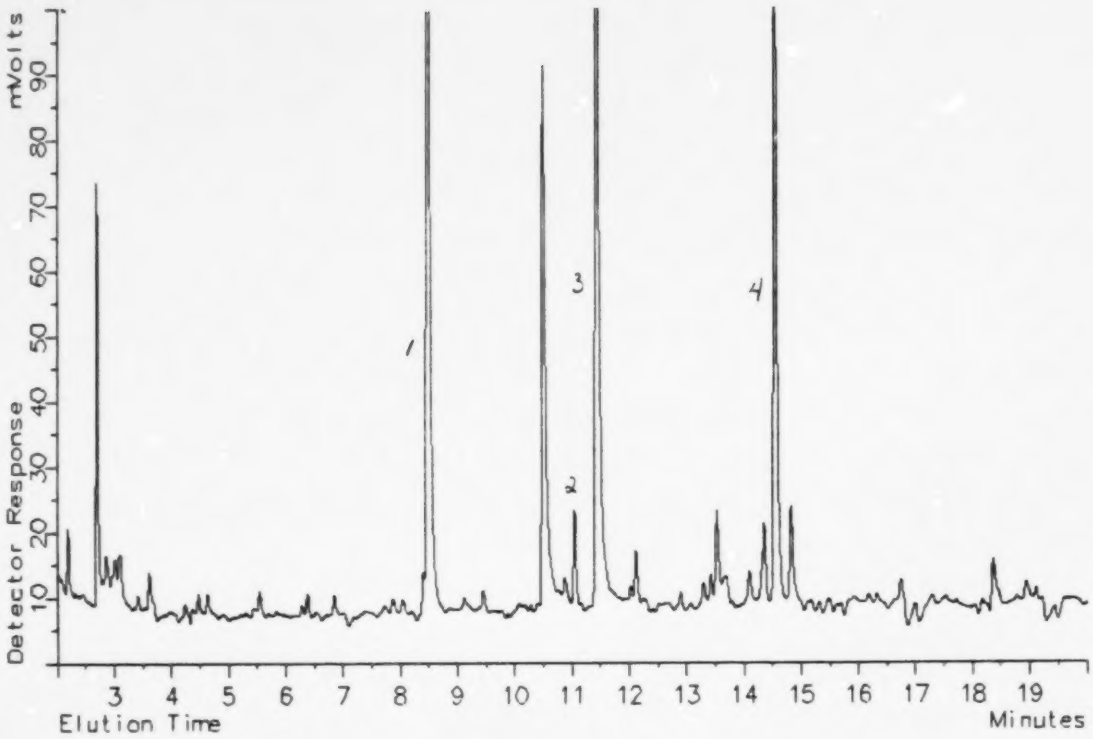


FIGURE 5.10. GC/ECD ANALYSIS OF PP 20 mL/min 8/3/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

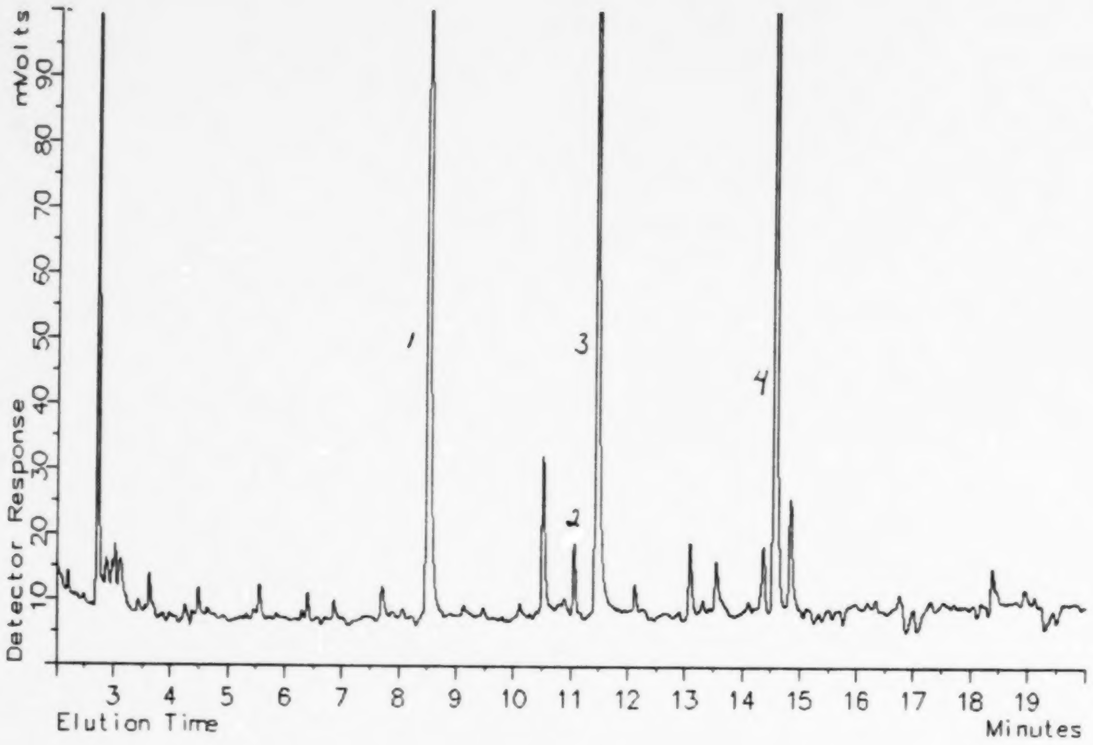


FIGURE 5.11. GC/ECD ANALYSIS OF PP 100 mL/min 8/3/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

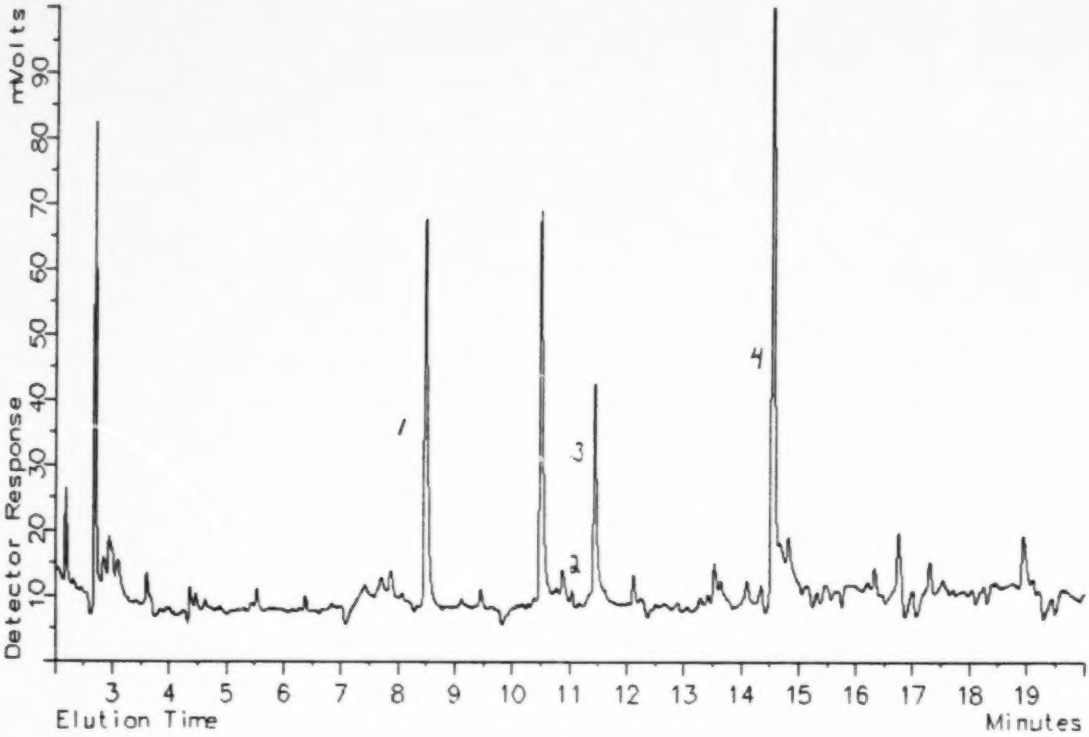


FIGURE 5.12. GC/ECD ANALYSIS OF PP SECTOR BLANK 8/3/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

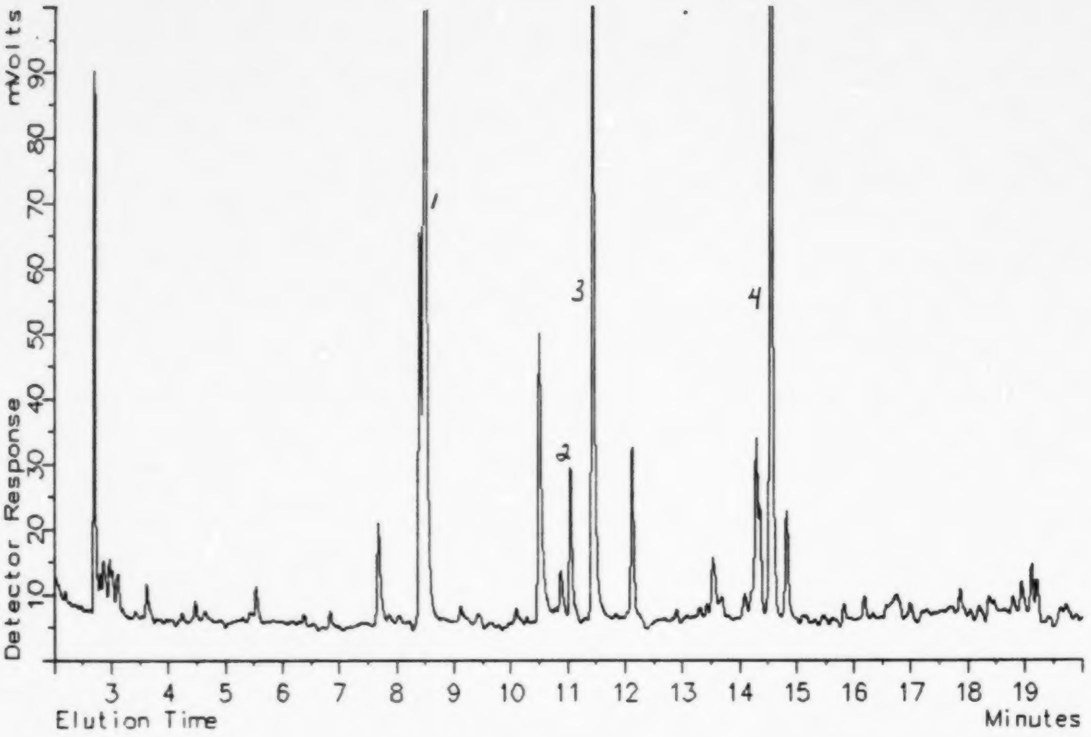


FIGURE 5.13. GC/ECD ANALYSIS OF PP 100 mL/min 8/4/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

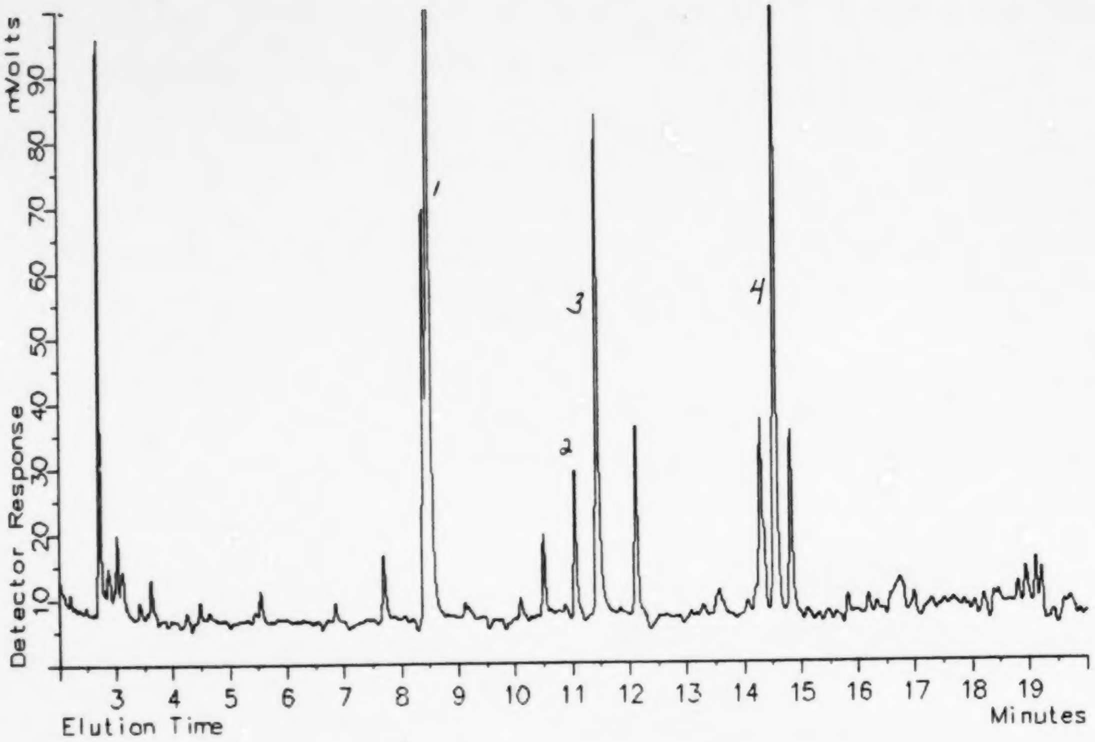


FIGURE 5.14. GC/ECD ANALYSIS OF RR 100 mL/min 8/6/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

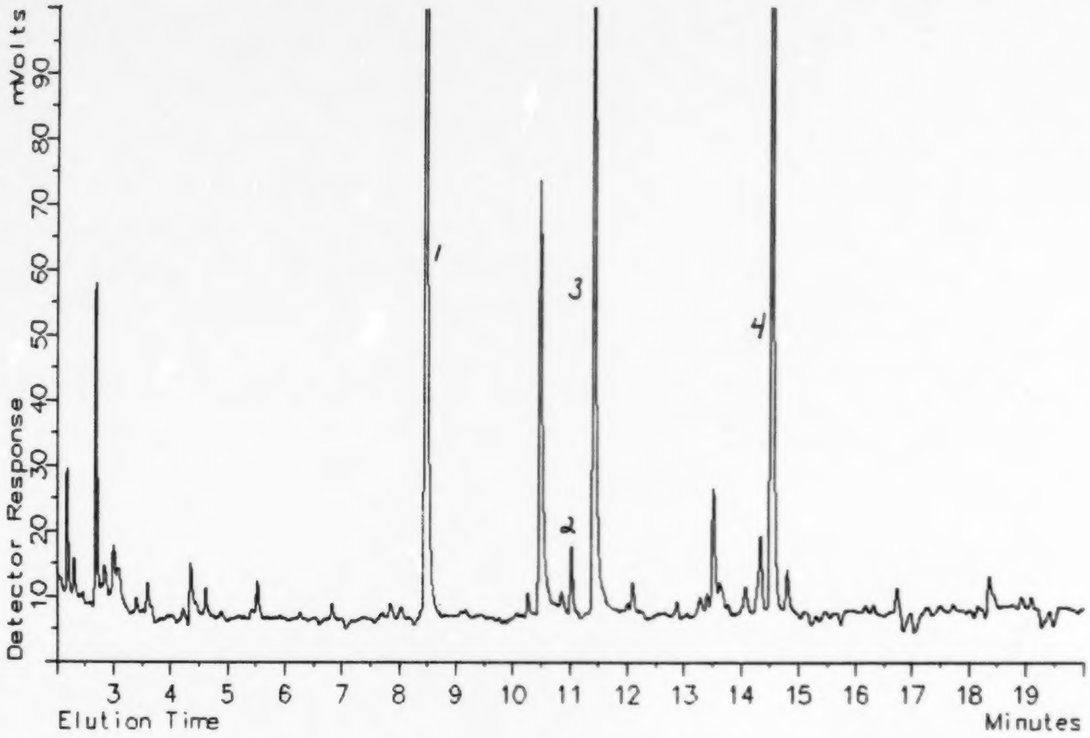


FIGURE 5.15. GC/ECD ANALYSIS OF RR 100 mL/min 8/7/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

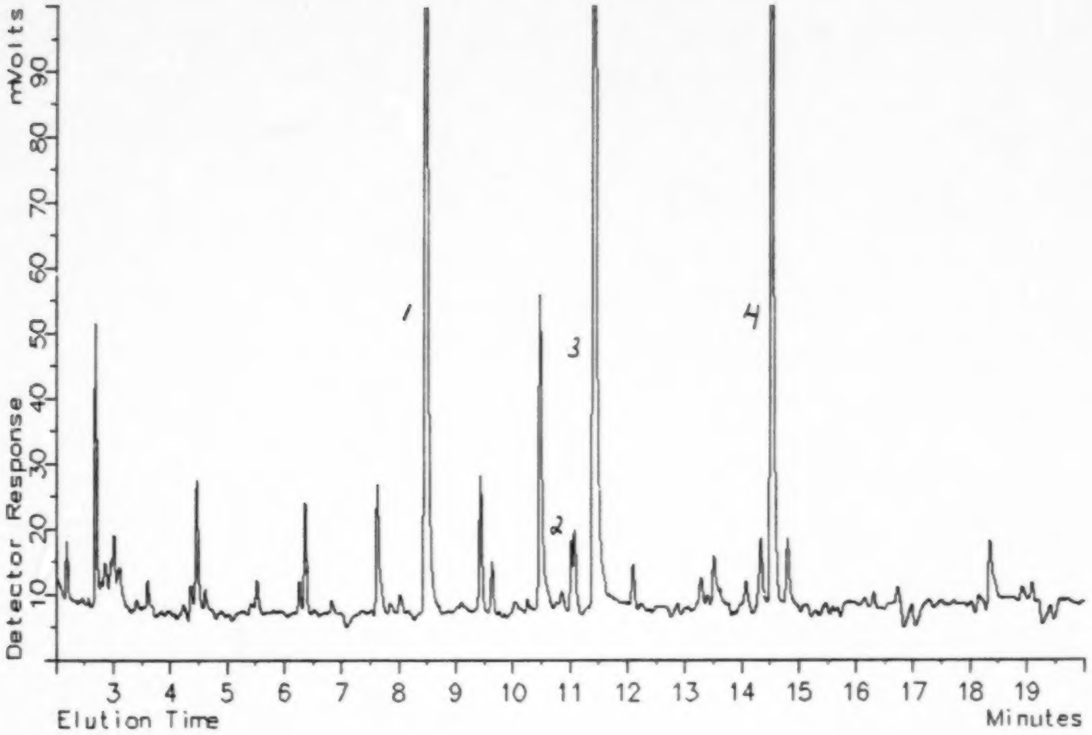


FIGURE 5.16. GC/ECD ANALYSIS OF RR FIELD BLANK 8/7/89 EXTRACT

Peak #	Identification	
1	2,4-diCl-phenol-d_3	methylated
2	2-NO_2-phenol-d_4	methylated
3	4-NO_2-phenol-d_4	methylated
4	DBOB (IS)	

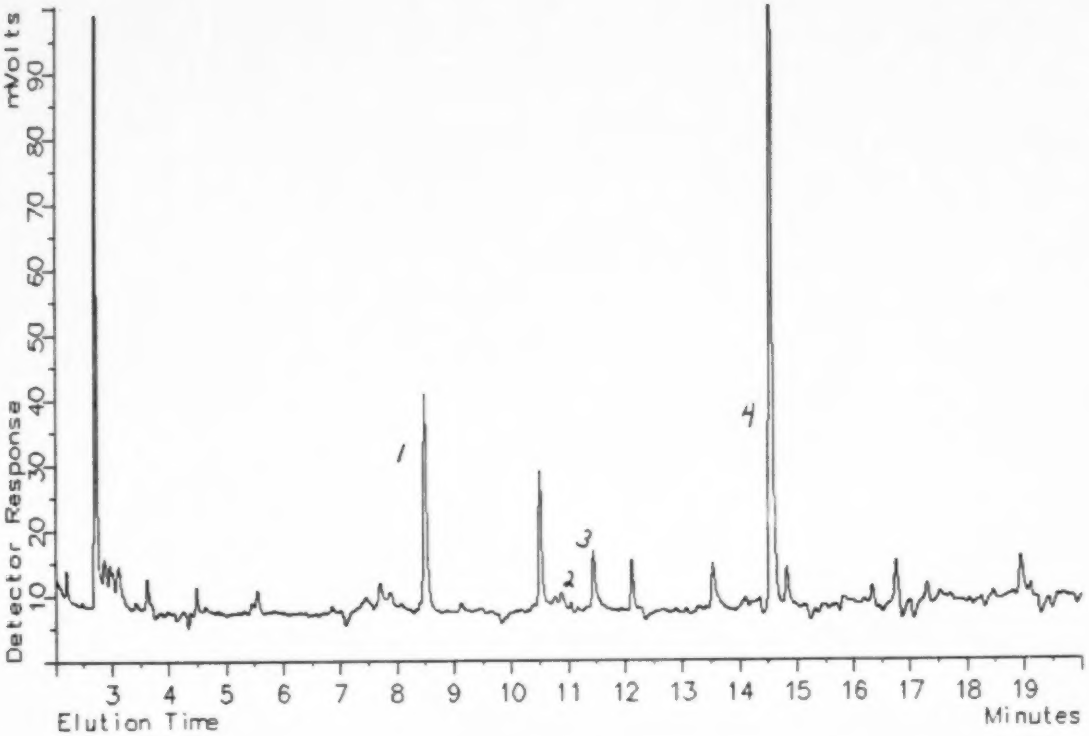


FIGURE 5.17. GC/ECD ANALYSIS OF RR SECTOR BLANK 8/7/89 EXTRACT

Peak #	Identification
1	2,4-diCl-phenol (methylated)
2	3-NO_2-phenol (methylated)
3	6-CH_3-2-NO_2-phenol (methylated)
4	2-NO_2-phenol
5	Dibromooctafluorobiphenyl (IS)
6	PentaCl-phenol (methylated)

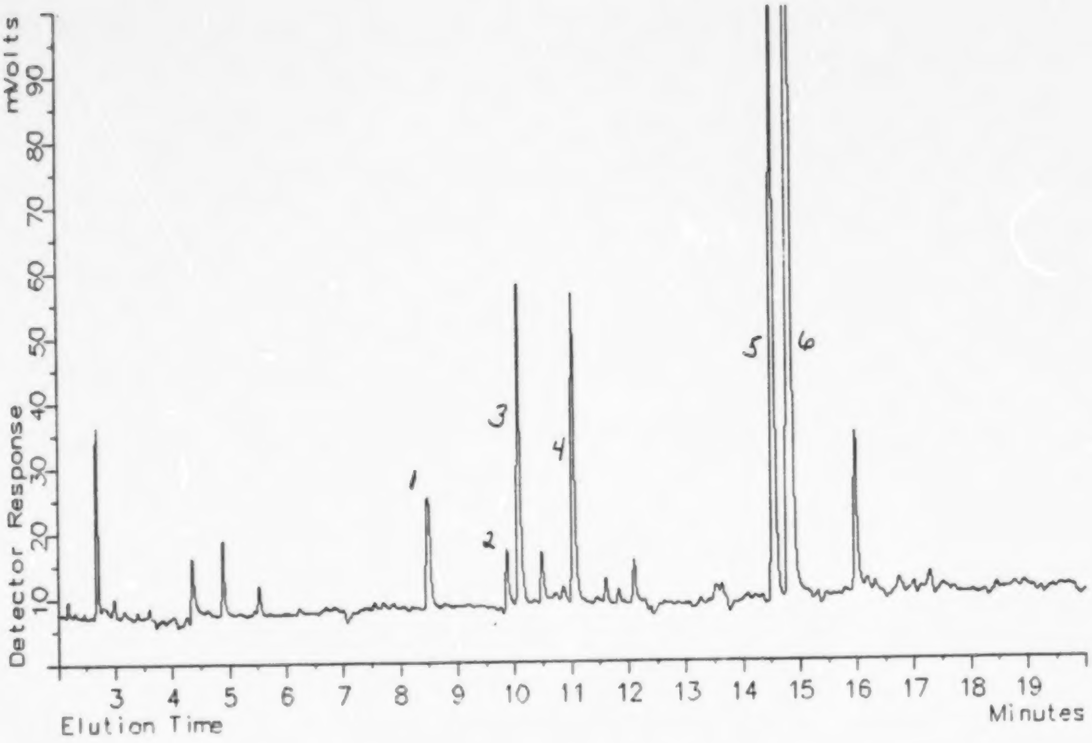


FIGURE 5.18. GC/ECD ANALYSIS OF 0.2 ng/µL PHENOL STD METHYLATED

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

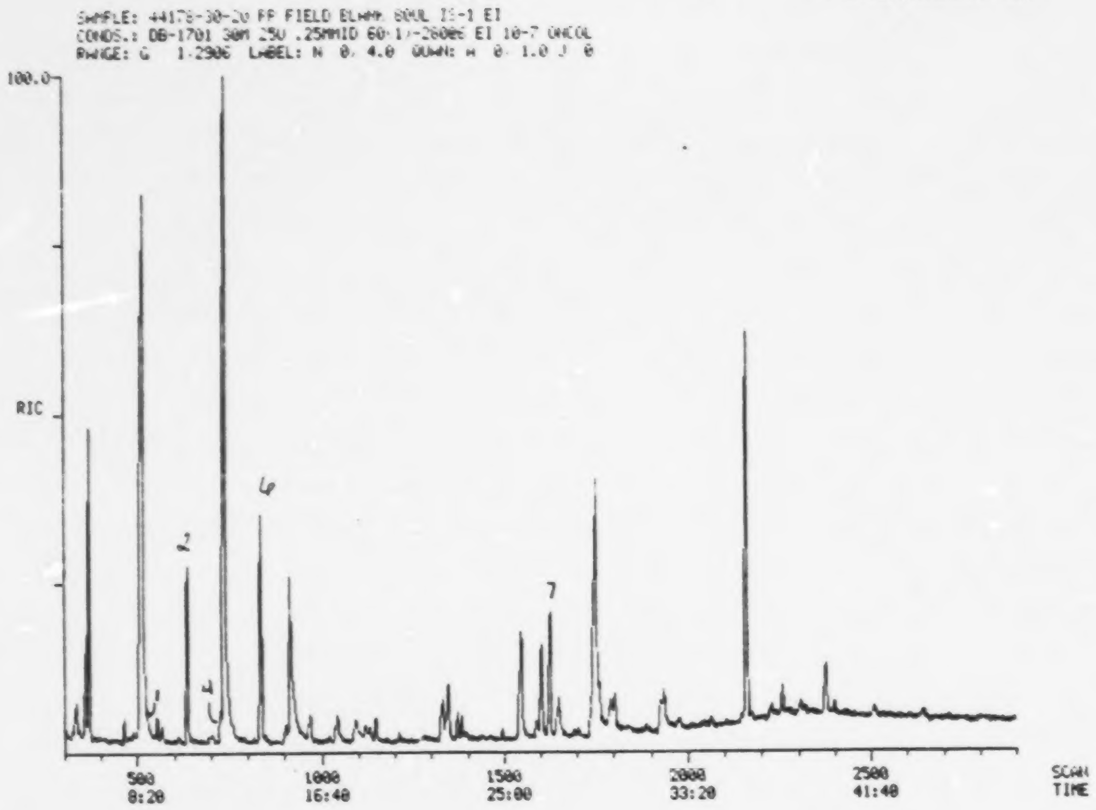


FIGURE 5.19. EI GC/MS ANALYSIS OF PP FIELD BLANK 8/3/89 EXTRACT

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

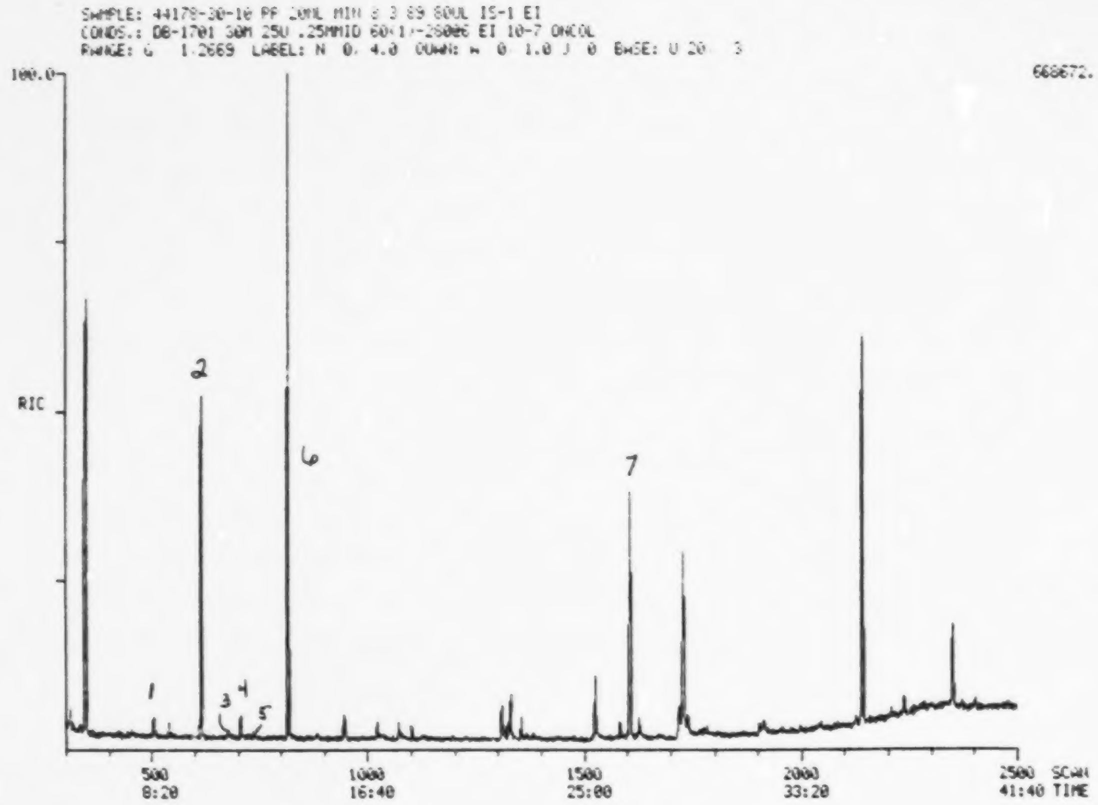


FIGURE 5.20. EI GC/MS ANALYSIS OF PP 20 mL/min 8/3/89 EXTRACT

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

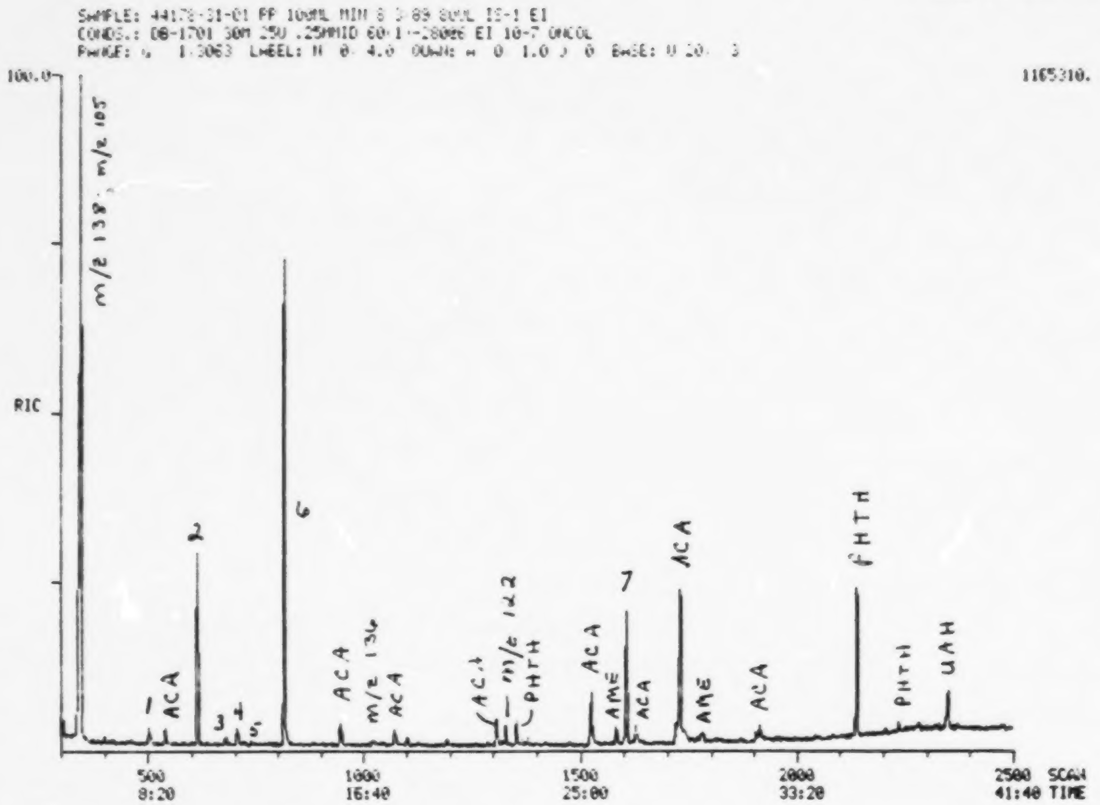


FIGURE 5.21. EI GC/MS ANALYSIS OF PP 100 mL/min 8/3/89 EXTRACT

(ACA-aliphatic carboxylic acid
PHTH- phthalate ester
AME- aliphatic methyl ester
UAH- unsaturated aliphatic hydrocarbon)

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

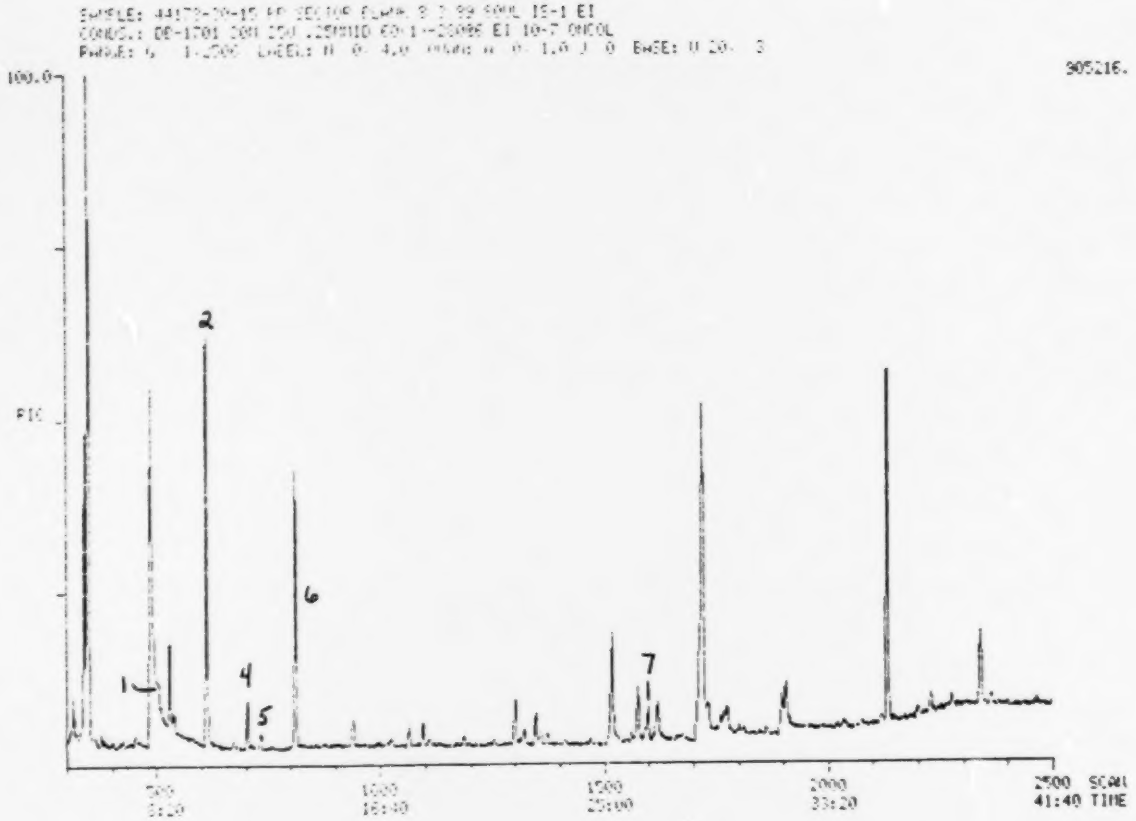


FIGURE 5.22. EI GC/MS ANALYSIS OF PP SECTOR BLANK 8/3/89 EXTRACT.

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

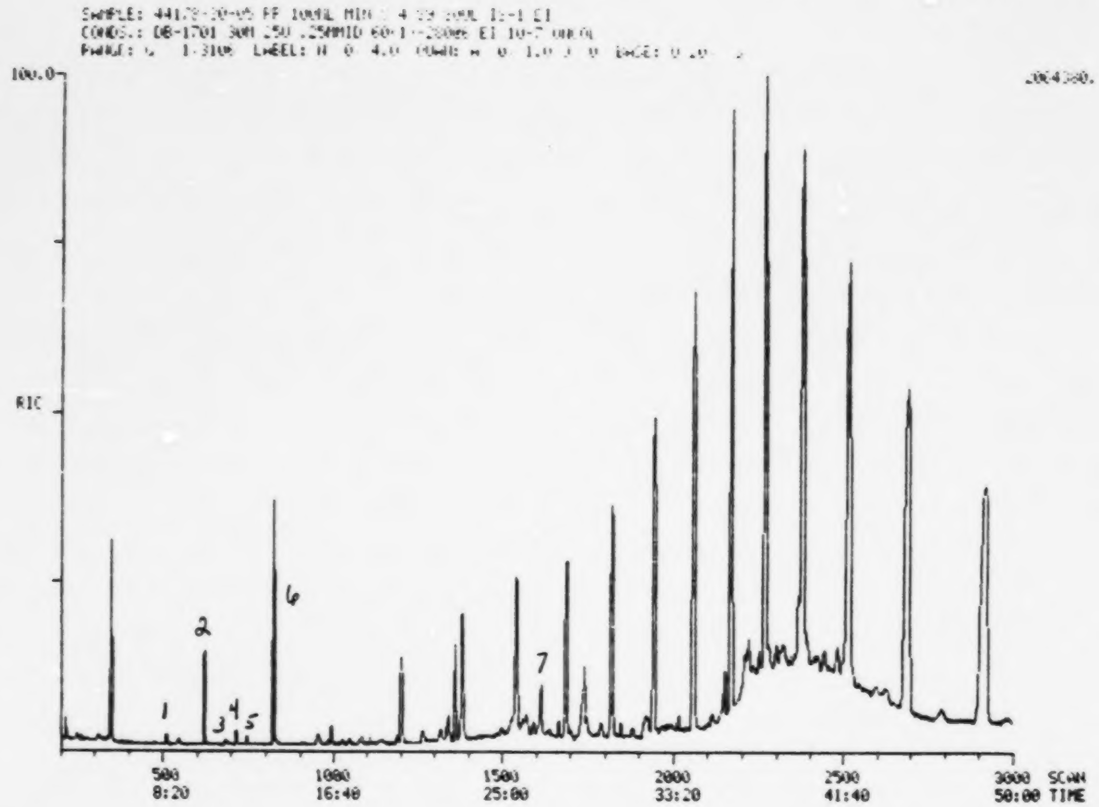


FIGURE 5.23. EI GC/MS ANALYSIS OF PP 100 mL/min 8/4/89 EXTRACT

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

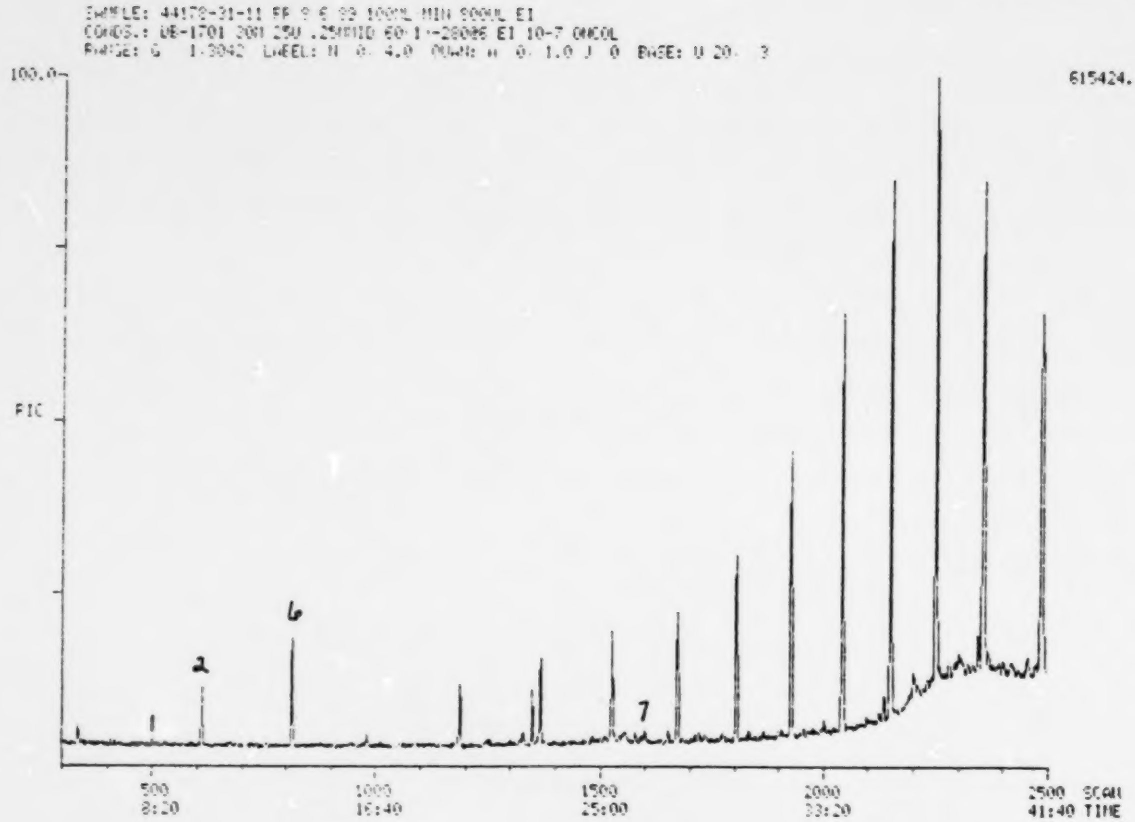


FIGURE 5.24. EI GC/MS ANALYSIS OF RR 100 mL/min 8/6/89 EXTRACT.

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

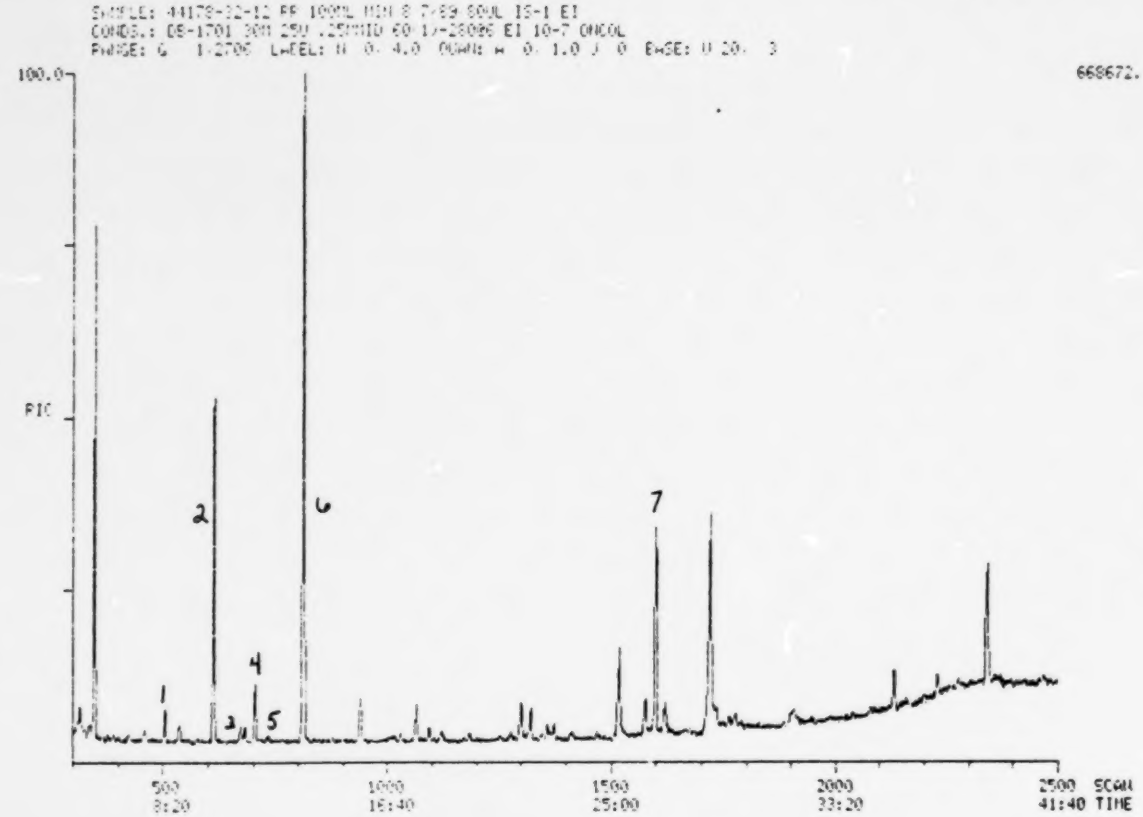


FIGURE 5.25. EI GC/MS ANALYSIS OF RR 100 mL/min 8/7/89 EXTRACT.

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

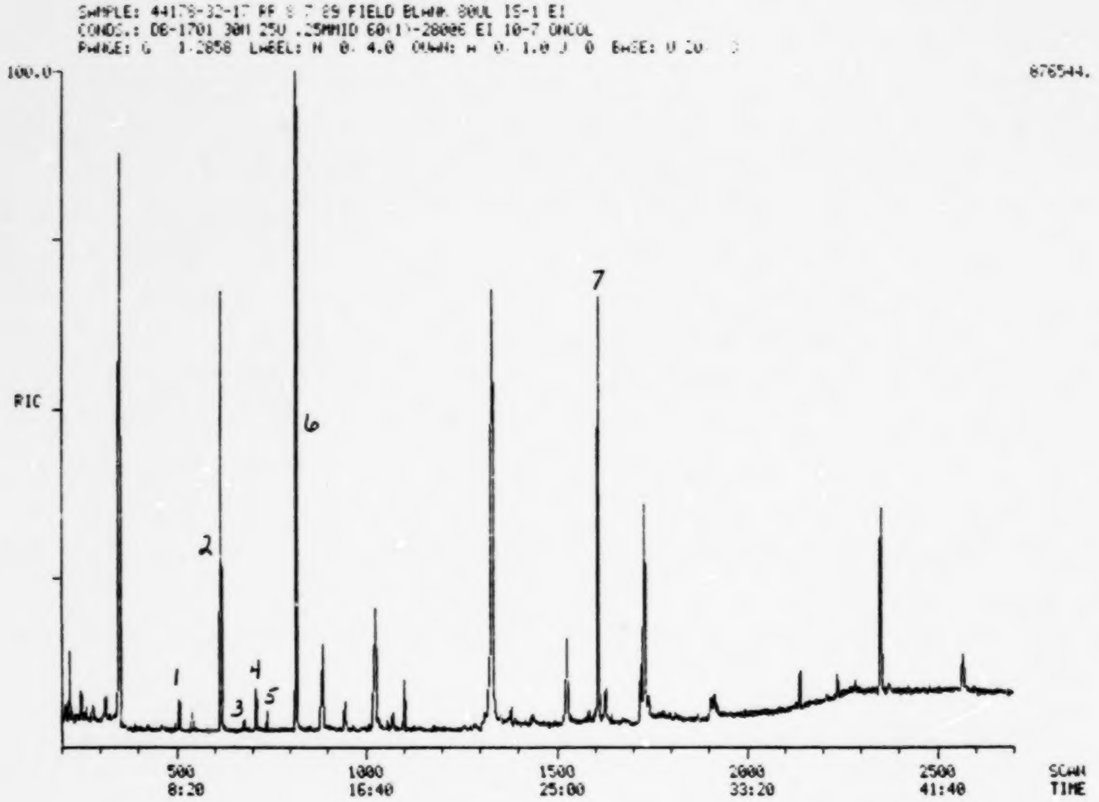


FIGURE 5.26. EI GC/MS ANALYSIS OF RR FIELD BLANK 8/7/89 EXTRACT

Peak #	Identification
1	2-Cl-phenol-d_4
2	Phenol-d_6
3	2-NO_2-phenol-d_4
4	Naphthalene-d_8 (IS)
5	4-CH_3-phenol-d_5
6	2,4-diCl-phenol-d_3
7	4-NO_2-phenol-d_4

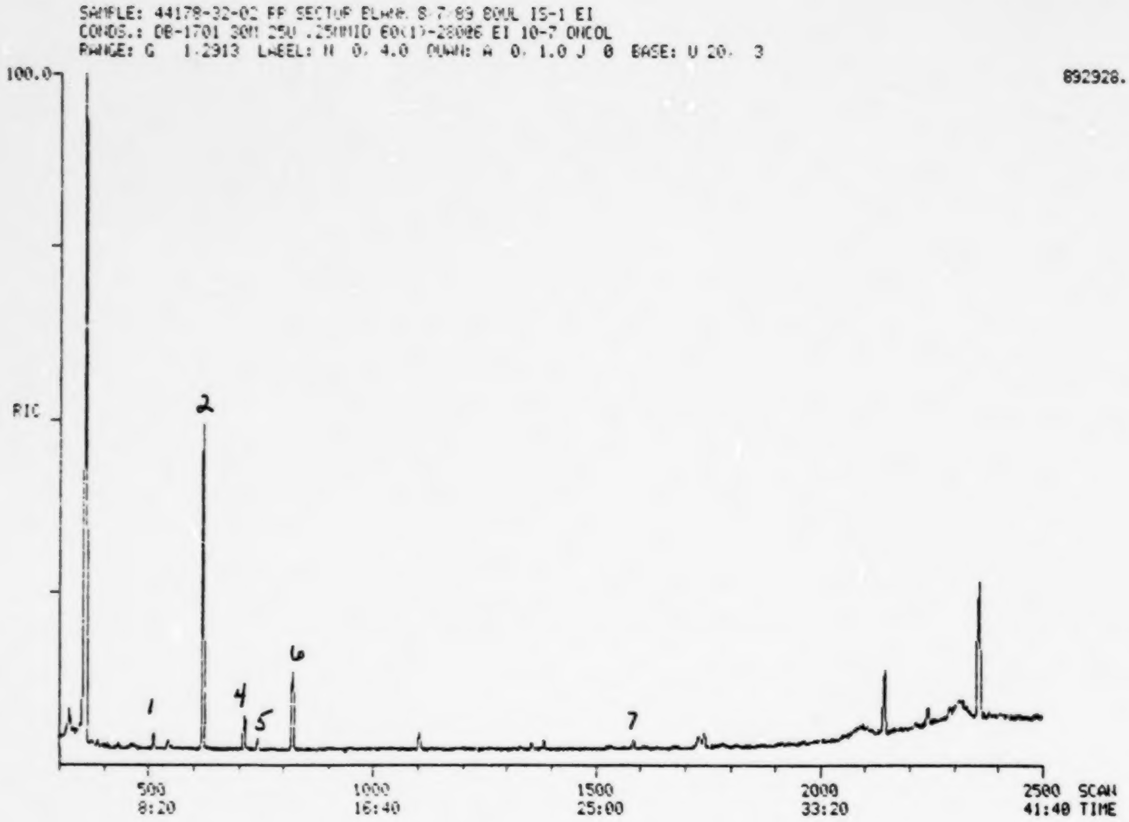
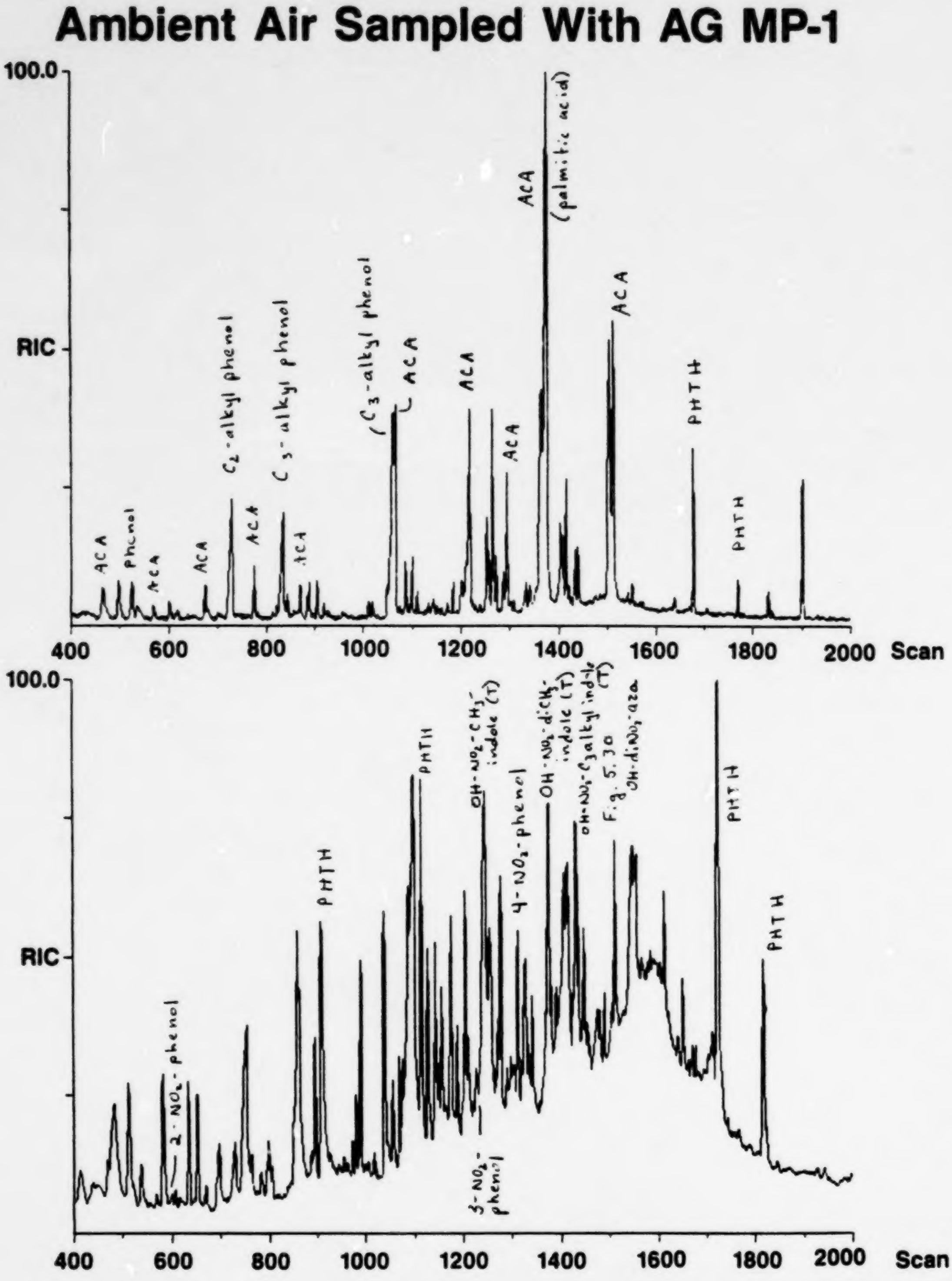


FIGURE 5.27. EI GC/MS ANALYSIS OF RR SECTOR BLANK 8/7/89 EXTRACT.



Ambient Air Sampled With AG MP-1

FIGURE 5.28. EI (TOP) AND NCI (BOTTOM) GC/MS ANALYSIS OF BATTELLE PARKING LOT - COLLECTED SAMPLES.

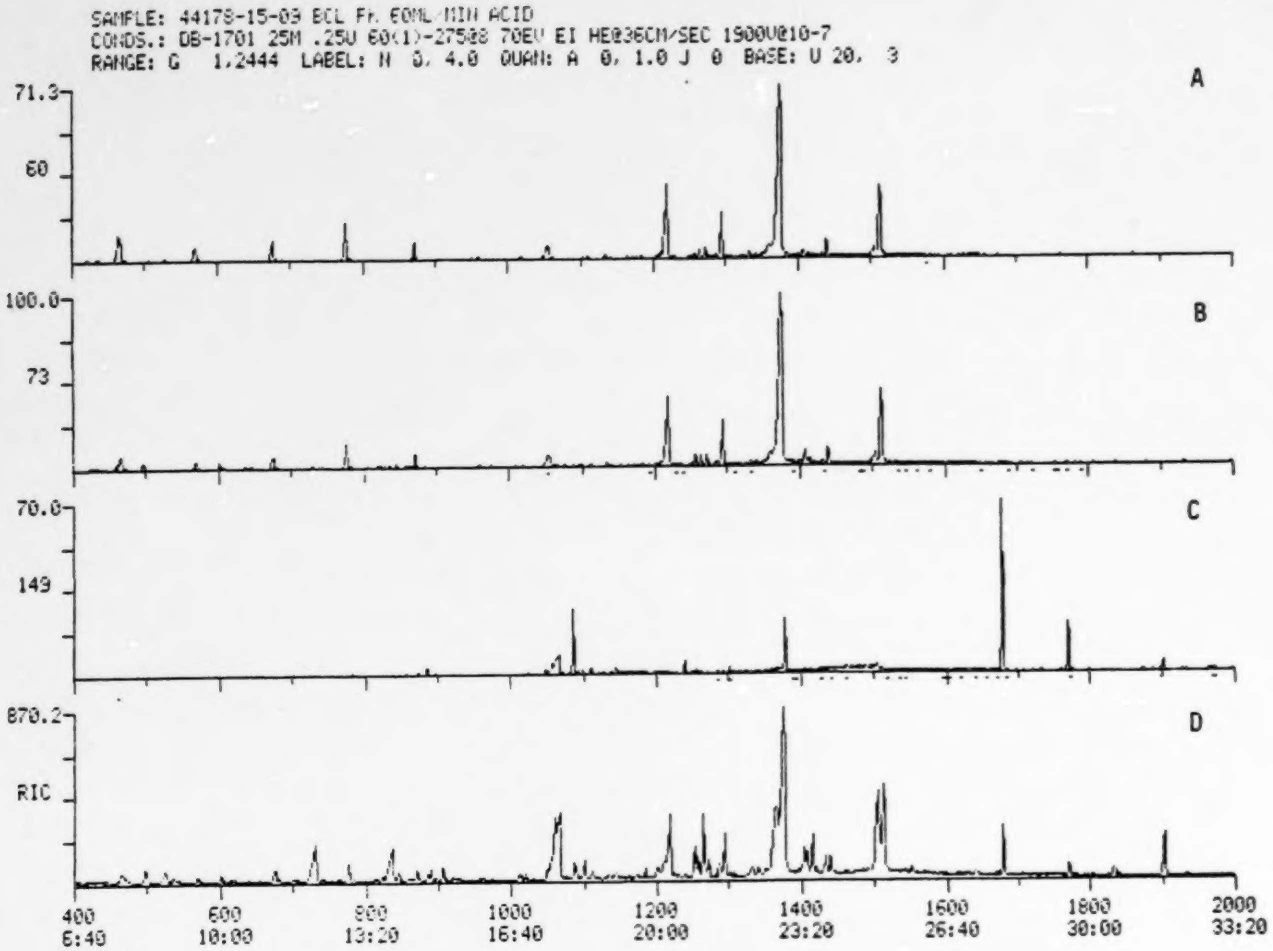


FIGURE 5.29. RELEVENT ION CURRENT CHROMATOGRAMS FOR COMPOUND CLASSES OF BATTELLE PARKING-LOT COLLECTED SAMPLE. ALIPHATIC CARBOXYLIC ACIDS (A&B), PHTHALATE ESTERS (C), TOTAL ION CURRENT CHROMATOGRAM (D).

Tentatively Identified OH-NO_2-AZA

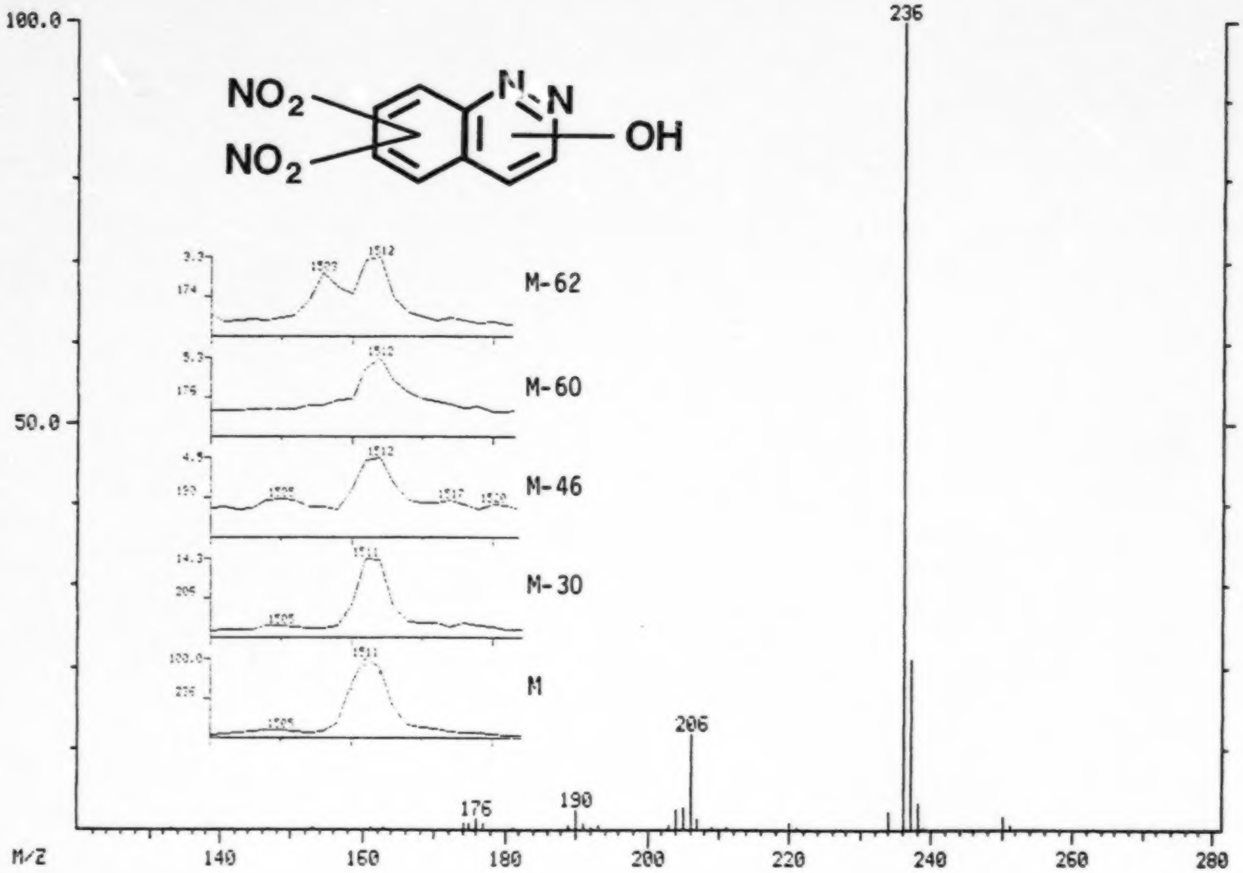


FIGURE 5.30. REPRESENTATIVE MASS SPECTRUM OF COMPONENT FROM NCI GC/MS ANALYSIS OF BATTELLE PARKING LOT SAMPLE; SPECTRUM #1511; INSET - RECONSTRUCTED ION CURRENT CHROMATOGRAMS FROM RELEVANT OH/NO_2 FRAGMENT IONS AND TENTATIVE STRUCTURE.

Peak #	Identification
1	Phenol-d_6
2	2-Cl-phenol-d_4
3	4-CH_3-phenol-d_5
4	2-NO_2-phenol-d_4
5	2,4-diCl-phenol-d_3
6	Naphthalene-d_8 (IS)
7	4-NO_2-phenol-d_4

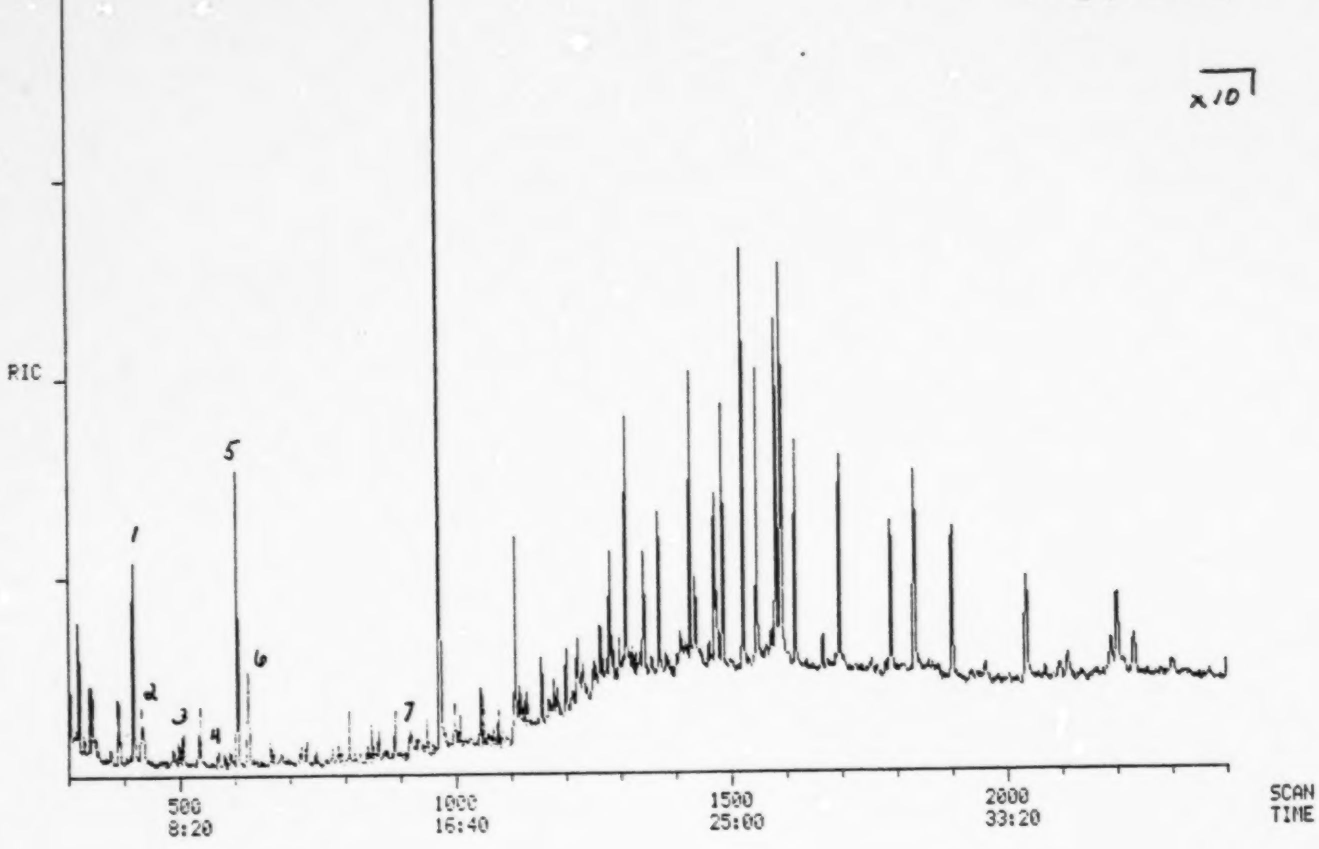


FIGURE 5.31. EI GC/MS OF COLUMBUS MUNICIPAL BUS GARAGE EXTRACT

Peak #	Identification
1	Phenol-d_6
2	2-Cl-phenol-d_4
3	4-CH_3-phenol-d_5
4	2-NO_2-phenol-d_4
5	2,4-diCl-phenol-d_3
6	Naphthalene-d_8 (IS)
7	4-NO_2-phenol-d_4

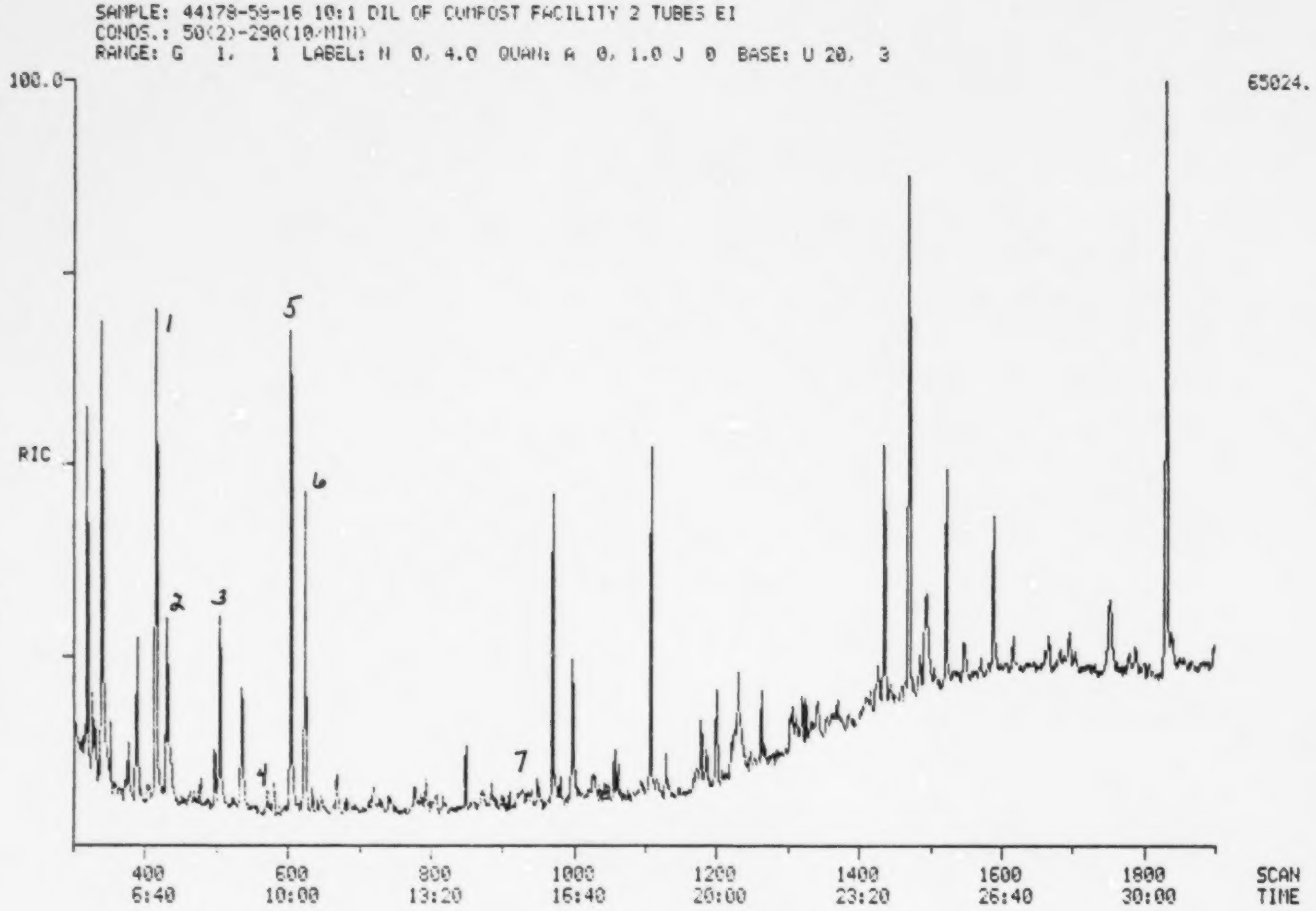


FIGURE 5.32. EI GC/MS ANALYSIS OF COLUMBUS MUNICIPAL COMPOSTING FACILITY EXTRACT

Peak #	Identification
1	Phenol-d_6
2	2-Cl-phenol-d_4
3	4-CH_3-phenol-d_5
4	2-NO_2-phenol-d_4
5	2,4-diCl-phenol-d_3
6	Naphthalene-d_8 (IS)
7	4-NO_2-phenol-d_4

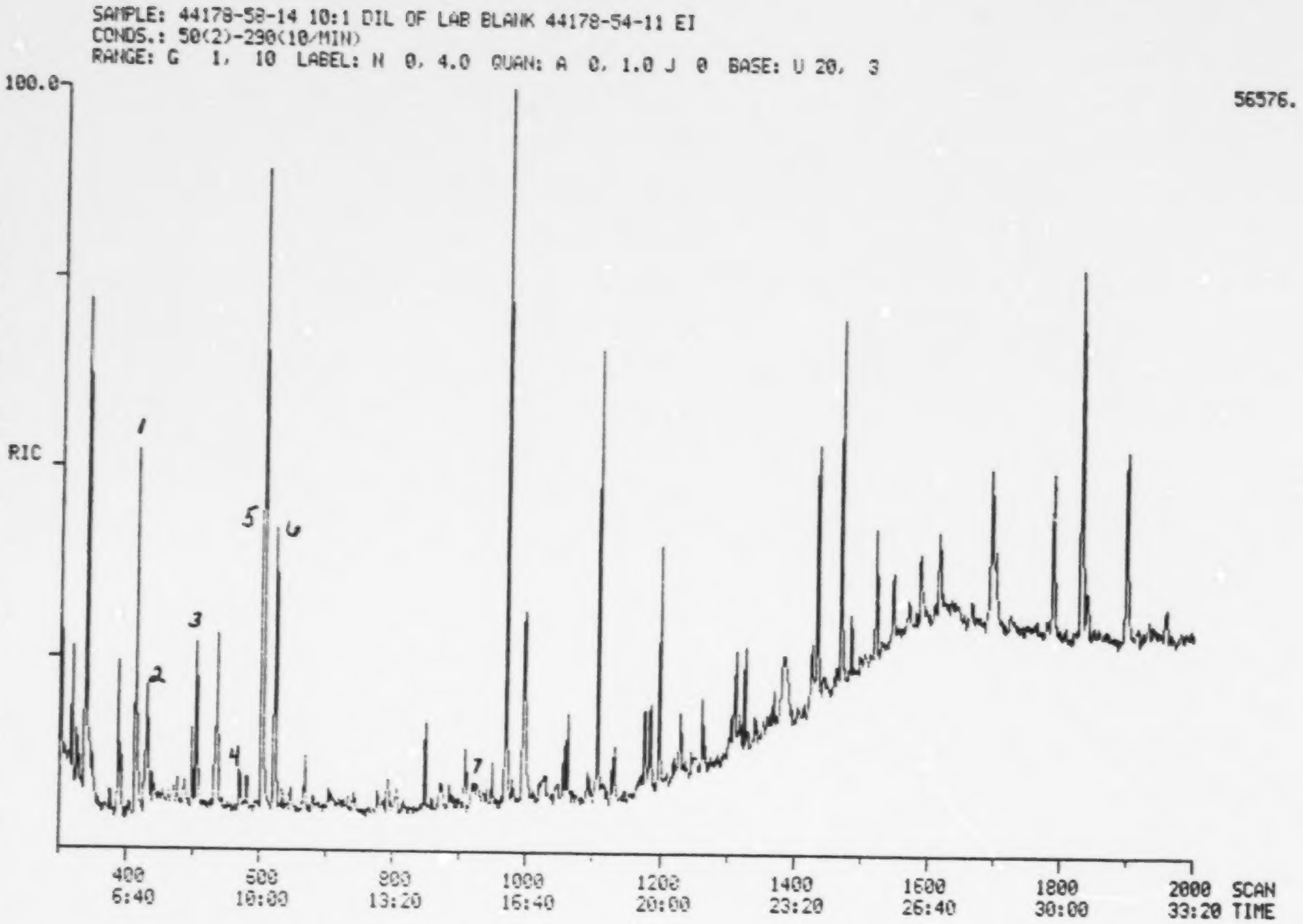
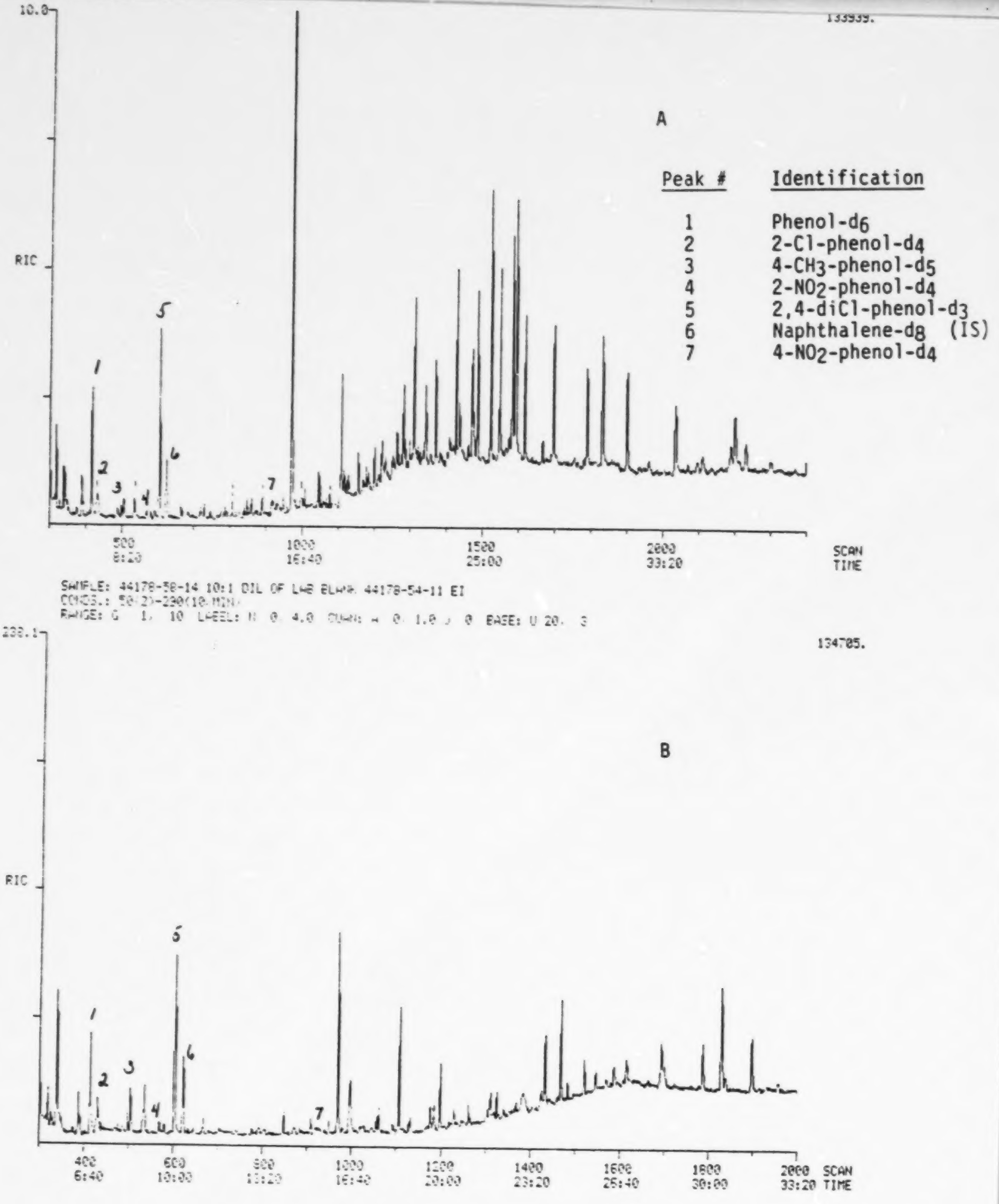


FIGURE 5.33. EI GC/MS ANALYSIS OF METHOD BLANK



Peak #	Identification
1	Phenol-d_6
2	2-Cl-phenol-d_4
3	4-CH_3-phenol-d_5
4	2-NO_2-phenol-d_4
5	2,4-diCl-phenol-d_3
6	Naphthalene-d_8 (IS)
7	4-NO_2-phenol-d_4

FIGURE 5.34. NORMALIZED CHROMATOGRAMS FOR MUNICIPAL BUS GARAGE (A) AND METHOD BLANK (B)

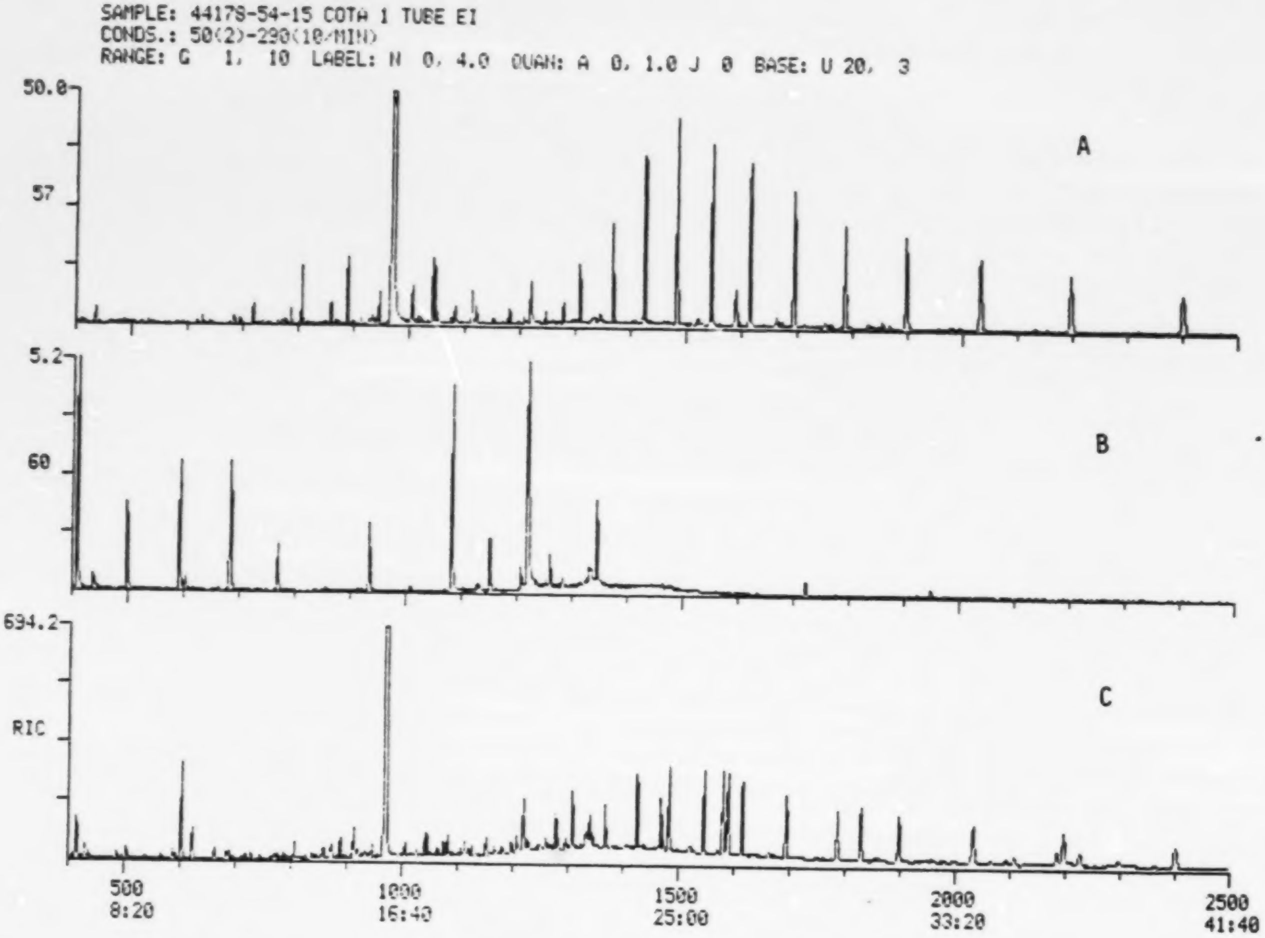


FIGURE 5.35. RECONSTRUCTED ION CURRENT CHROMATOGRAMS INDICATIVE OF ALIPHATIC HYDROCARBONS (M/Z 57; A) AND ALIPHATIC CARBOXYLIC ACIDS (M/Z 60; B) IN MUNICIPAL BUS GARAGE EXTRACT; TOTAL ION CURRENT CHROMATOGRAM (C).

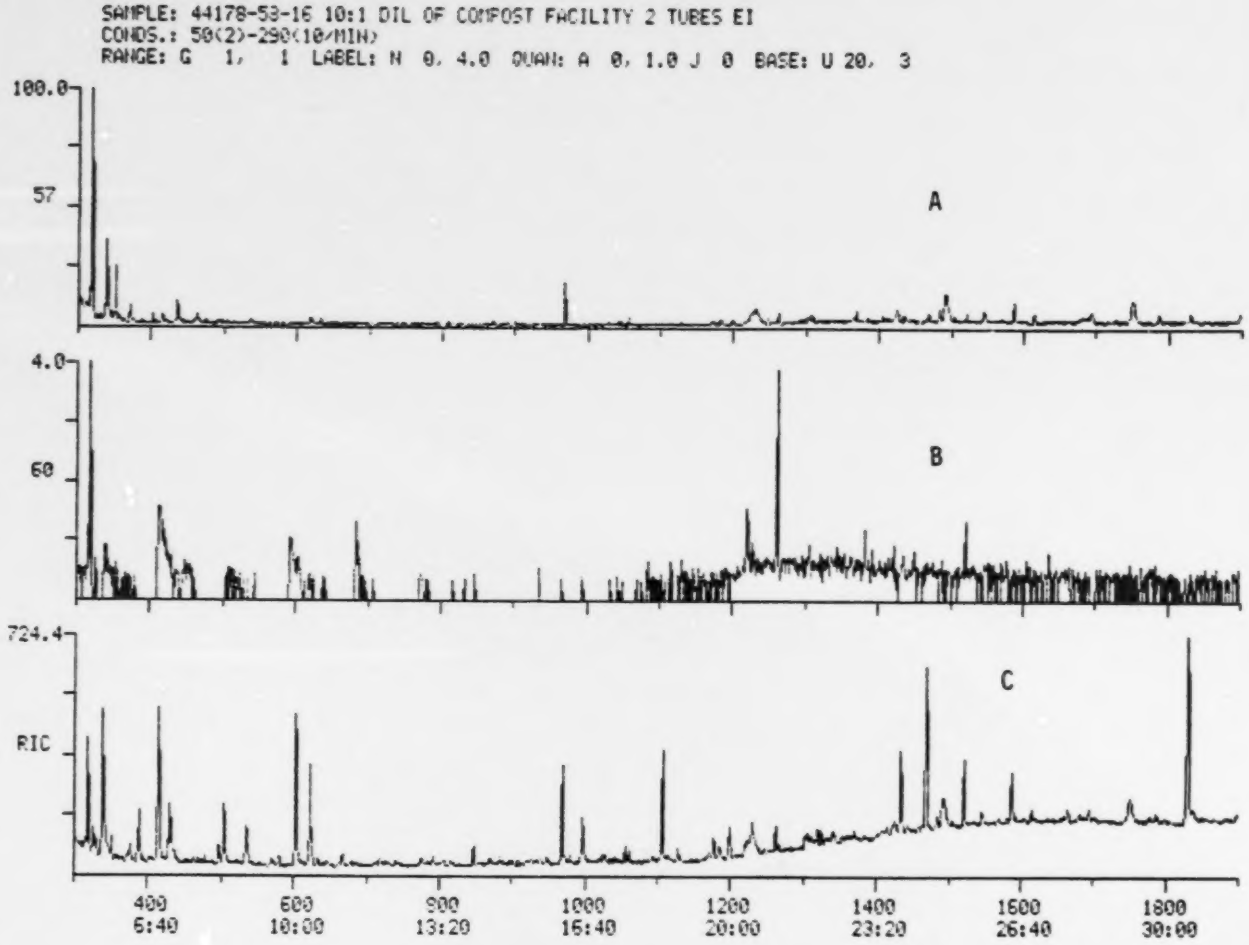


FIGURE 5.36. RECONSTRUCTED ION CURRENT CHROMATOGRAMS INDICATIVE OF ALIPHATIC HYDROCARBONS (M/Z 57; A) AND ALIPHATC CARBOXYLIC ACIDS (M/Z 60; B) IN MUNICIPAL COMPOST FACILITY EXTRACT; TOTAL ION CURRENT CHROMATOGRAM (C).

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